

DIFFERENT TYPES OF SPECTRA

1, continuous spectrum from an incandescent solid; 2, bright-line spectrum of sodium; 3, bright-line spectrum of mercury; 4, bright-line spectrum of calcium; 5, absorption spectrum of the sun, showing some of the strongest Fraunhofer lines. Note the coincidence of the bright lines for sodium in 2 and the dark lines *D* in 5

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Plate I

CHEMICAL SPECTROSCOPY

BY

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NEW YORK

JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

1939

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Printed in the U. S. A.

THE HADDON CRAFTSMEN, INC.,
CAMDEN, N. J.

PREFACE

The experimental portion of this book (Chapter XII) represents a development from mimeographed direction sheets used in connection with a course in "chemical spectroscopy" offered by the author at the Ohio State University. The interest in this course as expressed in the relatively large registration (30 to 50 students each year), and the lack of available material in English which would be suitable as a reference textbook, have prompted the preparation of this text and reference book.

Certain sections of this book, especially those dealing with apparatus and methods, have been prepared as a part of the author's contribution to the work of the American Society of Testing Materials committee on Spectrographic Analysis, of which the author is chairman of the sub-committee on Apparatus and Equipment.

The author is chairman of a committee of the Chemistry and Chemical Technology Division of the National Research Council on the Application of Spectroscopic Methods to Chemistry, and it is hoped that as a part of that committee's work some system of uniform recording and cataloging of absorption spectra data may eventually be evolved. The methods of recording absorption spectra data in this book are subject to revision and should not be considered as the approved systems of this committee. The committee would appreciate suggestions from interested workers on this subject and other problems in the field of chemical spectroscopy which might be worthy of consideration by this group.

ACKNOWLEDGMENTS

The author acknowledges help and guidance from certain of the more standard reference books in this field, including the works of W. Gerlach, G. Scheibe, F. Weigert, F. Twyman, A. C. Candler, H. E. White, H. Ley, D. M. Smith, and others, the tabular compilations of spectroscopic data such as Kayser-Konen, the International Critical Tables, Landolt-Bornstein, and Tables annuelles des constantes et données numériques, as well as from the authors of many articles and editors of journals for data used in the preparation of curves and tables for illustrative or reference purposes.

The author wishes to acknowledge grants in aid for research which have been made to him by the National Research Council, the American

Philosophical Society, the Society of Sigma Xi, the Eli Lilly Company, and others.

Acknowledgment of aid should be made to the John Simon Guggenheim Memorial Foundation for the grant of a fellowship for study on spectroscopic methods with Professor Hantzsch of the University of Leipzig, Professor Henri of the University of Zurich, and Professor E. C. C. Baly and Dr. R. A. Morton of the University of Liverpool, England.

For advice in the preparation of certain portions of this book and for illustrative material the author is pleased to acknowledge assistance from Professors H. P. Knauss, H. L. Johnston, L. L. Quill, F. A. Jenkins, R. B. Brode, C. E. Boord, G. R. Harrison, and D. H. Menzel; and to the Bausch and Lomb Optical Company, Eastman Kodak Company, Agfa Ansco Corporation, Adam Hilger, Ltd., Gaertner Scientific Company, Central Scientific Company, General Electric Company, Kipp and Zonen, Westinghouse, Hanovia, Dietert, and other individuals and concerns as indicated in the text.

Special acknowledgment is due to the Cellophane Division of the DuPont Company and to the American Crayon Company for the colored samples which are included in the back of this book for use in the experimental section. The author also acknowledges with thanks use of the color plate appearing as the frontispiece of this book. It is reprinted from S. R. Williams' "Foundations of College Physics," published by Ginn and Company.

It is a pleasant duty to acknowledge the cooperation of Miss Julia Appleton, who has assisted me in the preparation of the manuscript and figures and in the proofreading of this material, also to Miss Appleton and Miss B. J. Sipher for assistance in the preparation of the iron spectrum plates, and to Mr. Edwin Hodge for assistance in the preparation of certain figures and in proofreading.

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JANUARY 1939
OHIO STATE UNIVERSITY
COLUMBUS, OHIO

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CHEMICAL SPECTROSCOPY

CHAPTER I

INTRODUCTION

This book is intended to supply spectroscopic information to chemical workers, as well as to serve as a textbook for a course in chemical spectroscopy. Those workers who are interested in chemical spectroscopy as a profession will do well to cover the major portion of this book and certain of the important standard reference books which are listed in the bibliography. Those workers and students who wish a knowledge of chemical spectroscopy as a tool to interpret published data in their field of interest may not find it necessary to cover in detail all the chapters in this book. The following subdivisions of the book are suggested for certain fields of interest.

Qualitative and quantitative analysis of elements: Chapters I, III, IV, V, XII, XIII, and XIV for metallurgists, inorganic chemists, analysts, and those interested in the heavy chemical industries.

Absorption spectra of organic and inorganic compounds: Chapters I, III, VI, VII, VIII, and XII for organic chemists, biochemists, medical research workers, and those concerned with special inorganic applications or dye chemistry.

A set of twelve experiments on the application of spectrographic methods (Chapter XII) follows the theoretical discussion. A number of tables and charts for the solution of these experiments and for general use in the interpretation and application of spectroscopic methods have been included.

THEORY OF LIGHT

The accepted theory of the nature of light is a combination of many earlier theories, including Newton's corpuscular theory (1666), the wave theory of Huygens (1673), the electromagnetic theory of Maxwell (1860), and the more recent work of Hertz, Lorentz, and Planck. The fusion of these theories provides for a corpuscular form of energy (quantum) propagated in a wave form (*A 15, A 78*). From the simple theory of wave

motion we can indicate the essential characteristics of light. In Fig. 1.1 the distance from *A* to *B* represents the length of a complete wave or cycle, and is known as the wavelength of the light. The number of these complete cycles or waves in a unit length (*C* to *D*) will be known as the wavenumber. If *Y* is a fixed point in space, past which the wave front is moving, then the number of complete cycles or waves passing this point in a given time will be known as the frequency of the light.

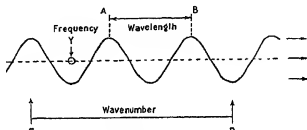


Fig. 1.1.—Graphical indication of the relation between wavelength (λ), wavenumber (ν'), and frequency (ν).

Wavelength (λ) = distance between *A* and *B*.

Wavenumber (ν') = number of waves in unit length (*C*–*D*).

Frequency (ν) = number of waves passing a fixed point (*Y*) in a unit time.

By consulting Fig. 1.2 one can form some conception of the dimensions of the light wave and its relation to the other vibrating forms of energy propagation. In this figure the space between *A* and *B* represents the photographic range, i.e., the spectral region over which the photographic plate will give a direct response to light rays (not including x-rays). The narrower dark band between *A* and *B* represents the portion of the photographic spectrum which produces the sensation of visible light.

In the indication of the relation between wavelength, wavenumber, and frequency, we may use the following notations:

$$\frac{1}{\text{WAVELENGTH}} \quad \text{WAVENUMBER} = \frac{\text{FREQUENCY}}{\text{SPEED OF LIGHT}}$$

Using the terms λ for wavelength, ν' for wavenumber, ν for frequency, and c for the speed of light we obtain the expression

$$\frac{1}{\lambda} = \nu' = \frac{\nu}{c}$$

The speed of light has been shown to be constant over the spectral range with which we are concerned, and in meters is expressed as 2.99796×10^8 meter (or 10^{10} cm) per sec, in vacuum. For accurate physical work it is quite essential to correct light measurements for the variation in the density of the medium through which the light passes, or in which it is

RADIANT ENERGY UNITS

measured. For most of the necessary chemical measurements, especially those dealing with absorption spectra and qualitative and quantitative emission analysis, we can deal with tables prepared from data observed in air at standard conditions, or even ignore the necessary correction where the probable error of the work exceeds this correction. In general, we express c as 3×10^{10} cm per sec rather than the value 2.99796×10^{10} .

SPECTRAL DISTRIBUTION OF ENERGY

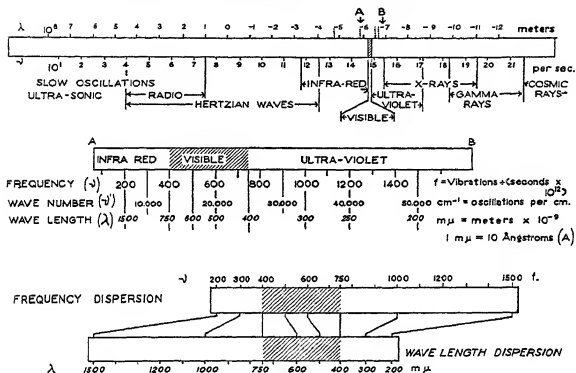


FIG. 1.2.—Spectral distribution of radiant energy.

The limits in wavelength of the visible spectrum are found by observation to be between 4×10^{-7} and 7.5×10^{-7} meter. The accuracy with which the earlier workers could determine wavelength values within this region (see Chapter IV) justified the use of a number with four significant figures in front of the decimal point, so that the limits of the visible spectrum might thus be indicated as from 4000×10^{-10} to 7500×10^{-10} meter. The unit of measurement in this system was called an angstrom after the Swedish physicist, Ångström, and is now defined as $1/6438.4696$ of the wavelength of the cadmium red line, rather than one ten thousand millionth ($1/10,000,000,000$) of a meter. The increase in accuracy of modern physical methods has enabled us to measure wavelength values to an accuracy of one part in about ten million, or to about four significant figures after the decimal point in the angstrom system of notation.

In many of the data published on the absorption spectra of organic compounds and visible color, the accuracy of the work does not justify the use of more than three significant figures, and in the infrared the wavelength values increase to such a size that the use of the angstrom

TABLE 1.1
DEFINITION OF IMPORTANT UNITS

LIGHT

Wavelength, λ

Angstrom, A, \AA , or \AA = $1/6438.4696$ of the wavelength of the Cd red line
= meters $\times 10^{-10}$

Millimicron, $m\mu$ = meters $\times 10^{-3}$

Micron, μ = meters $\times 10^{-6}$

Wavenumber, ν'

Waves per centimeter = cm^{-1}

Frequency, ν

Fresnel, f = vibrations per (second $\times 10^{-12}$)

Interrelation between above units

$1/\lambda = \nu' = \nu/c$ c = speed of light = 3×10^{10} cm per sec

Example of interconversion

$1/\lambda$ in $m\mu \times 10^7 = \nu'$ in cm^{-1} ; ν' in $\text{cm}^{-1} \times 3 \times 10^{-2} = \nu$ in f
e.g., $400 m\mu = 1/400 \times 10^7 = 25,000 \text{ cm}^{-1}$; $25,000 \text{ cm}^{-1} = 3 \times 10^{-2} \times 25,000 = 750 f$

ABSORPTION SPECTRA

I_0 = incident intensity

I = transmitted intensity

I/I_0 = transmission or transmission factor (T)

$1 - T = A$ = absorption; [reflection (R) is equivalent to transmission (T)]

$T \times 100$ = per cent transmitted or transmittancy (t)

$I = I_0 \cdot 10^{-kcd}$, where c = concentration in grams per liter, and d = thickness in centimeters

$\text{Log } I_0/I = kcd$ = extinction (E)

$k = E/cd$ = specific extinction

$\text{Log } E = \text{log extinction}$

ϵ = molecular extinction = $k \times \text{molecular weight}$

unit would become awkward. Hence, one finds a variety of wavelength terms depending upon the spectral region and character of the data considered. For reasons which will be discussed later (Chapters II and IX), one finds it convenient, with certain forms of data, to use frequency and

wavenumber values rather than wavelength. This is especially true in the assignment of energy levels in atomic spectra, and the determination of series relationships in absorption spectra (*A13*, *A73*, *B14*, *B20*).

RECOMMENDED SYSTEM OF RECORDING ABSORPTION SPECTRA CURVES

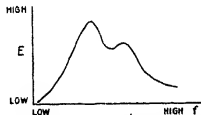


FIG. 1.3a.—Recommended method of plotting extinction against frequency (f).

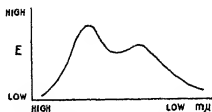


FIG. 1.3b.—Recommended method of plotting extinction against wavelength ($m\mu$).

Use only k , E , ϵ , $\log E$, or $\log \epsilon$ as ordinate and plot in increasing values to the top.

Use f (fresnel) for frequency and plot with increasing values to the right, i.e., ultraviolet on the right and infrared on the left.

Use $m\mu$ for wavelength and plot with increasing values to the left, i.e., ultraviolet on the right and infrared on the left.

The reader may note that the author has not been consistent, either in this book or his published articles, in the system of notation which he has used. In many of the published articles the author has conformed to the systems used in the laboratories in which the measurements were made. So far as this book is concerned, an attempt has been made to acquaint the reader with the various systems in use, and, in some cases, to compare their application in the presentation of the same or similar data.

POSITIVE AND NEGATIVE SPECTROGRAMS

There is no common agreement among spectroscopists as to the proper method for the presentation of spectrum photographs or the reproduction of spectrograms in published data. A spectroscopist should be adept at mental inversion of black and white so as to compare positive and negative spectrograms. A *positive spectrogram*, **P**, is defined as a spectrogram in which the lines or bands appear as white, with a black background representing those portions of the spectrogram in which there is no radiant energy. A *negative spectrogram*, **N**, is defined as a spectrogram in which the lines or bands appear as black, with a clear or white background representing those portions of the spectrogram in which there is

no radiant energy. The negative spectrogram is similar to the photographic negative obtained with a spectrograph; the positive appears as the contact print of such a negative. Since there may be some confusion as to whether a positive or negative spectrogram is reproduced the symbols **P** and **N** have been inserted in the titles to figures to indicate the corresponding positive and negative character of the spectrogram. See Chapter XIII for special methods of producing positive and negative spectrograms.

LITERATURE

Note: A list of books and articles in the fields of *general spectroscopy* (A), *absorption spectra* (B), and *research publications* (C) is to be found in the Bibliography (pages 315 to 325). Reference to books and articles in this list are made by letter and number, e.g., (A26), (C17), etc.

General

"Spectroscopy in Science and Industry." S. Judd Lewis (A47).

"Measurement of Radiant Energy." W. E. Forsythe and others (A15).

"Metallurgical Analysis by the Spectrograph." D. M. Smith (A63).

Reference

Bragg (A5), Fabry (A13), Gibson (B14), Weigert (A73).

CHAPTER II

ATOMIC AND MOLECULAR SPECTRA

The discussion in this chapter is an elementary presentation of the theory of atomic and molecular spectra. Although some understanding is helpful, the complete comprehension of the theory of spectra, or even of the material in this chapter, is not essential to the use of spectroscopic methods in many chemical problems. In particular, workers in the fields of organic and biochemistry with problems dealing with absorption spectra data may find little of advantage to them in this chapter.

In this review discussion no attempt has been made to give complete references, but a selected bibliography will be found at the end of the chapter to which the reader may refer for further information.

ORIGIN OF SPECTRA

Excited atoms or molecules are known to emit light of definite wavelength values, and the dispersion of this light by a spectroscope or spectrograph produces a spectrum which is characteristic of the atom or molecule. The means of excitation may be an arc, spark, flame, or discharge tube. The production of emitted light or radiant energy results from the falling of electrons into lower levels of the atom. These electrons have been pushed into outer levels by an excitation force. The energy (E), which is evolved, may be represented as the difference in energy of the two electronic states, and may be indicated by the equation

$$E = E_2 - E_1 = h\nu$$

where E_1 represents the total energy of the molecule in the lower electron state, and E_2 the total energy of the molecule in the higher electron state. This difference may be equated to $h\nu$, where h is the Planck constant and ν the frequency of the light which is emitted. One may thus measure energy in terms of frequency of emitted light, just as one may also measure energy in calories or volts. Since each spectrum line is the result of energy lost by the excited atom, it follows that, if light is the exciting medium, absorption of light of a similar wavelength may take place as a means of exciting an atom.

As has been demonstrated by theoretical and experimental work, this emission and absorption of energy takes place in accordance with fixed and well-defined rules. The electron which has been forced away from

the proton can be forced only to certain predetermined positions, and the return of the electron to its normal position can take place only through a certain number of finite moves, i.e., it may make the complete change in one move or it may return to an intermediate level and from there to its stable or normal level.

HYDROGEN SPECTRUM

The simplest atom is hydrogen, and it will serve as an excellent example of these effects. The hydrogen spectrum as observed (Fig. 2.1) appears

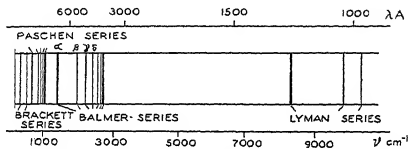


Fig. 2.1.—Hydrogen spectrum. (See also the hydrogen Balmer series in the flash spectrogram, Fig. 4.1.)

to be composed of a number of lines which may be arranged in a series as indicated. From the Grotrian diagram (Fig. 2.2) it can be seen that these lines are related to a series of levels which may be represented as increasing voltage or frequency on the energy ordinate. It is to be noted that the greatest energy is required to move the electron from its stable position (first level) to the second level, and, as would be expected in the separation of two oppositely charged bodies, as one increases the separation, the energy required becomes increasingly less and less until at last the electron is completely removed from the atom shells and ionization is said to have occurred.

The various spectral series which are to be found in the hydrogen spectrum may be classified in accordance with the electron level to which the electron returns, or, in absorption, to the electron level from which the electron was dislodged. The Balmer series which includes the visible lines of the hydrogen spectrum thus represents the return of electrons from other, higher levels to the second level. It should be noted that an electron in a higher level may return to a lower level through several different paths, i.e., an electron in the fourth level may return to the third (Paschen series, line 18,751), thence to the second level (Balmer series, line 6562), and finally to the first level (Lyman series, line 1215). It may also go directly to the first level from the third level and avoid the second level (Lyman series, line 1025); or it may go directly to the second

level from the fourth level and avoid the third level (Balmer series, line 4861). The course to be followed by the returning electron is influenced by the exciting conditions, which result in markedly different spectra as observed in the arc and spark excitation of certain elements.

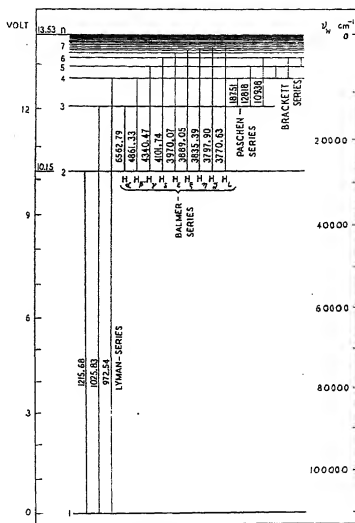


FIG. 2.2.—Energy-level diagram of hydrogen; vertical lines indicate electron jumps. The electron jump from a higher to a lower level causes an emission line of the wavelength indicated on each line.

These levels or terms may be incorporated into an equation as first suggested by Balmer, in the form

$$\nu = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R is a constant with the value $109,677.76 \text{ cm}^{-1}$, and n_1 and n_2 are the numbers of the final and initial electron states respectively. By the use of this formula the spectrum lines for the Balmer series (final term = 2, and variable terms = 3, 4, 5, 6, etc.) can be calculated as shown in

Table 2.1. Graphically one may represent this by plotting the term values from R/∞ (dissociating term) to $R/4$, against frequency, which will give

TABLE 2.1
BALMER SERIES OF HYDROGEN LINES

n_2	ν Calculated	λ Calculated	λ Observed
α 3	15,233.15 cm^{-1}	6564.62 Å	6564.60
β 4	20,564.76	4862.68	4862.68
γ 5	23,032.53	4341.68	4341.68
δ 6	24,373.05	4102.89	4102.89
ϵ 7	25,181.34	3971.19	3971.19

a uniform slope for the points of intersection of the frequency values with the corresponding term values (Fig. 2.3).

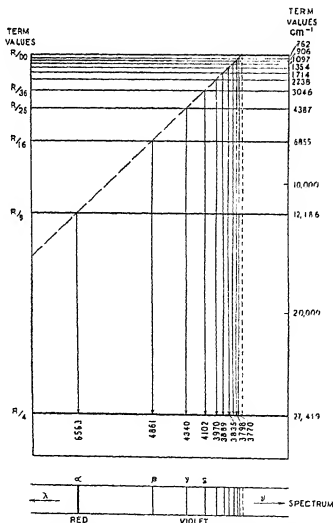


FIG. 2.3.—Level diagram of the Balmer series. The lower projected spectrum is on a uniform frequency scale. After Candler (*A 6*).

SPECTRAL TERMS

In the spectra of elements involving only one electron such as hydrogen, ionized helium, and the second ionized spectra of lithium, one would expect the same type of spectra. This expectation has been confirmed by experimentation. With more complicated atoms the possible series overlap to a much greater extent since the removal of one electron does not so greatly alter the remaining negative charge or electron content, and hence the energy values are of a lower order of magnitude.

The various series of lines in the spectra of elements with more than one electron are often distinguished by their appearance, and hence the designations of sharp, principal, diffuse, and fundamental have been used. The identification of series may be made in accordance with certain properties. For example, the lines of the principal series will be apparent in the absorption spectrum produced by the element in a vapor state and are usually subject to reversal, i.e., self-absorption due to absorption of the light by cooler vapors surrounding the hot spark or arc. Other properties which may be used to clarify the assignment of the series and terms include such effects as the Zeeman effect, excitation potential, Stark effect, and Paschen-Bach effect.

Rydberg has developed a general formula for these series which may be expressed as $\nu = \nu_1 - R/(m + a)^2$, where a is a constant characteristic of the series, and m is a series of integral series values. R , known as Rydberg's constant, is constant for practically all series, and ν is the frequency of the limit of the series. It is thus possible to indicate each series' value by a definite quantum formula although for each series and element the value a will be different. A less precise, but more generally applicable, method is to indicate the changes in levels or terms by a code system of notation or classification. In this system of classification developed by Paschen and Götze, the lowest terms of the four series corresponding to the sharp, principal, diffuse, and fundamental are indicated by the terms $1S$, $2P$, $3D$, and $4F$, respectively. The higher terms in each of these series will then be indicated by mS , mD , mF , where m is an integer and greater than the numerical prefix of the term to which the electron falls.

In accordance with this system of notation the spectrum line series may be indicated as

Principal series	$mP - 1S$	where $m = 2, 3, 4, \dots$
Sharp series	$mS - 2P$	where $m = 3, 4, 5, \dots$
Diffuse series	$mD - 2P$	where $m = 3, 4, 5, \dots$
Fundamental series	$mF - 3D$	where $m = 4, 5, 6, \dots$

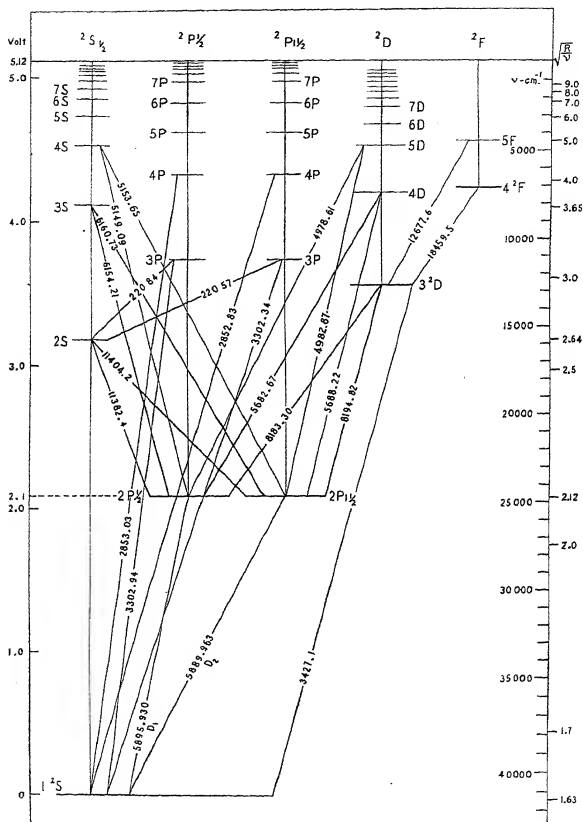


FIG. 2.4.—Level diagram of sodium. After Grotrian, *Graphische Darstellung der Spektren* (A21). In the more precise nomenclature the normal level $1^2S_{1/2}$ is designated by the normal electron state of $3s$ as the 3^2S state (normal state). See Table 2.4 (A77).

A more precise system of nomenclature which is generally accepted in the theoretical analysis of spectral terms (*A77*) designates the ground term in accordance with the assigned electron configuration (see Table 2.4). Since the earlier system of nomenclature has been used in less technical discussions (*C125a*) (*A6*) it has been used in this brief description of atomic spectra.

For example, in Fig. 2.4 the first line of the principal series may be indicated as $2P - 1S$, which involves a change of state from the $2P$ term, or level, to the $1S$ level. As will be noted in Fig. 2.4, there are certain limitations of combinations, such as the combination of terms with only those series on either side, i.e., an S term combines only with a P term, P terms combine only with S or D , and D terms only with P and F terms. Spectral terms may be of a simple singlet type or more complex doublet, triplet, or higher multiplet types. To designate this, one adds a superscript prefix of 2, 3, etc. (as 2P , 3P , etc.), to the term values to indicate this doublet, triplet, or higher system, and a subscript suffix of 0, $\frac{1}{2}$, 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, etc. (as P_0 , $P_{1/2}$, etc.), to indicate sublevels. In Fig. 2.4, $m^2P_{1/2} \rightarrow 1^2S_{1/2}$ indicates the lower-frequency, and $m^2P_{3/2} \rightarrow 1^2S_{1/2}$ the higher-frequency, components of the principal series of doublets of which the yellow D lines are the first members. In the sharp and fundamental series this separation between doublets is constant on a frequency scale, and the separation of the doublets in the principal and diffuse series is associated with the separations of the sharp and fundamental series although the separation is not constant.

Fowler summarizes the definition of these series as follows:

1. The sharp series exhibits a constant difference in wavenumbers in the doublet types with the higher-frequency line showing a weaker intensity. Since a constant difference is shown between doublet pairs, the limiting frequency of these doublet series will be different by this amount, but the value, a , of Rydberg's formula will be constant.

2. The principal series exhibits a reverse in the intensity ratio as compared with the sharp series, in that the higher-frequency component has the greater intensity. In the first members the difference in the doublet pair is the same as in the sharp series, but the higher members show decreasing differences so that the limiting frequency values of both series of doublet lines are the same. This involves in the Rydberg formula a constant, ν_1 , and a variable, a .

3. The diffuse series is somewhat complex, involving lines showing the separations of the sharp and fundamental series. The three lines may be considered as two pairs having one line in common (that of the higher-wavenumber component). The middle component is the strongest and is separated from the low-wavenumber component, which is the weakest in

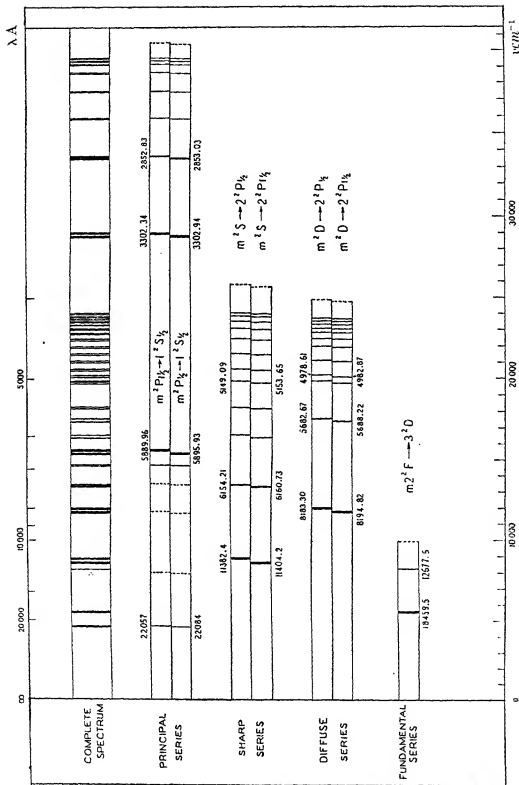


FIG. 2.5.—Series in the sodium spectrum (on a uniform frequency scale) and the combination of these series to form the completed spectrum.

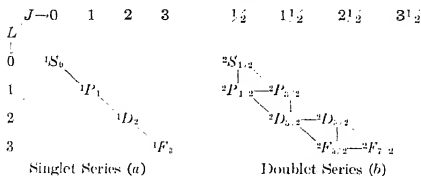
intensity, by the frequency difference of the fundamental series. The lines may be indicated as α , β , and γ , α being the component of highest frequency. The β line approaches the γ line at the series limit so that but two lines appear at the limit. Furthermore, the limits of the diffuse series are the same as those of the sharp series.

4. The fundamental series in a doublet multiplicity involves pairs of lines with a constant separation equal to the β - γ interval in the first of the diffuse series group of lines.

5. Additional series are possible, of course, but little is known of their characteristics. Such levels are indicated as G , H , etc.

The explanation of why the separate term levels should be split into components of slightly different energy content is based on an angular momentum, which is expressed as J , where J may equal $\frac{1}{2}$, $\frac{3}{2}$, etc., in even multiplicities, or 0, 1, 2, etc., in odd multiplicities. In spectral theory, L is used to indicate the orbital and J the electronic angular momentum. Where there is but one electron outside the nucleus or core, the remaining electrons and proton forming a completed octet, J can have but two values: $(1 + \frac{1}{2})$ and $(1 - \frac{1}{2})$. The terms of the doublet spectrum can best be indicated by Table 2.2 (b). Here the lines indicate

TABLE 2.2
TERM DIAGRAM



the observed transitions which are presented graphically in the Grotrian diagram of the sodium spectrum (Fig. 2.4). With regard to intensities of lines, Sommerfeld has shown that the strongest lines are produced when both L and J are changed in the same direction (165).

SPECTRAL TERMS AND THE PERIODIC TABLE

In the foregoing discussion we have dealt with the spectra of hydrogen and the alkali metals. The elements in any group or subgroup in the periodic table exhibit similar spectra, but with increasing complexity as

one goes across the periodic table. In the second group in the periodic table (alkaline-earth metals), the spectra are characterized by the presence of singlet and triplet systems, involving as before the principal, sharp, diffuse, and fundamental series. The next periodic group (B, Al, etc.), the trivalent group with three electrons in the outer shell, gives spectra showing doublets and quartets. In the next periodic column, singlets, triplets, and quintets occur, and thus the maximum values increase in succeeding columns in the periodic table until octets are produced. The J values for the electronic angular momentum for odd spectral series (singlets, triplets, quintets, etc.) will be found to be even values differing by unity, while in the even series (doublets, quartets, etc.) the electronic angular momentum values (J) will be found to equal unit values less $\frac{1}{2}$.

The classical Bohr theory assigns to the atom a certain number of shells, and all the electrons in each shell have the same series quantum number, i.e., for the K shell the series quantum number, $n = 1$; for the L shell, $n = 2$; for the M shell, $n = 3$; etc. Each shell has been divided into subshells in accordance with the number of s , p , d , and f electrons present. Orbital quantum numbers, l , have been assigned to each of these subshells as indicated in Table 2.3.

TABLE 2.3
ASSIGNMENT OF ELECTRONS IN SHELLS

Shell	K	L		M			N			$O, P, \text{etc.}$
Quantum number (n)	1	2		3			4			
Subshell	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$
Quantum number (l)	0	0	1	0	1	2	0	1	2	3
Number of electrons.	2	2	6	2	6	10	2	6	10	14

It is thus possible to classify the elements of the periodic table in accordance with their electron configuration and predict the character of the spectra and the normal states of each atom. For example, hydrogen has one electron of the $1s$ state, and in accordance with the rules which have been discussed it will have a normal state of $^2S_{1/2}$ (odd numbers of electrons will have J values equal to $\frac{1}{2}$ or $\frac{1}{2} + \text{a unit value}$, and the multiplicity will be doublet for Group I of the periodic table). Helium, on the other hand, has two s electrons in the $n = 1$ shell which are indicated as $1s$, and hence a normal state, 1S_0 .

The second period of the periodic table involves the L shell. For all these members the K shell is complete and hence all atoms will have a

common part in their configuration of $1s^2$. The electron configurations may be indicated as in Table 2.4.

TABLE 2.4

PARTIAL TABLE OF ELECTRON CONFIGURATION OF THE ELEMENTS

(For a complete table, see White, (A77) p. 82; Candler, (A6) p. 194; etc.)

Atomic No.	Element	Shells				Normal State
		K ($n = 1$) $l = 0$	L ($n = 2$) $l = 0, 1$	M ($n = 3$) $l = 0, 1, 2$	N ($n = 4$) $l = 0, 1, 2, 3$	
1	H	$1s$				$^2S_{1/2}$
2	He	$1s^2$				1S_0
3	Li	$1s^2$	$2s$			$^2S_{1/2}$
4	Be	$1s^2$	$2s^2$			1S_0
5	B	$1s^2$	$2s^2 \ 2p$			$^2P_{1/2}$
6	C	$1s^2$	$2s^2 \ 2p^2$			3P_0
7	N	$1s^2$	$2s^2 \ 2p^3$			$^4S_{3/2}$
8	O	$1s^2$	$2s^2 \ 2p^4$			3P_2
9	F	$1s^2$	$2s^2 \ 2p^5$			$^2P_{3/2}$
10	Ne	$1s^2$	$2s^2 \ 2p^6$			1S_0
11	Na	$1s^2$	$2s^2 \ 2p^6$	$3s$		$^2S_{1/2}$
12	Mg	$1s^2$	$2s^2 \ 2p^6$	$3s^2$		1S_0
13	Al	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p$		$^2P_{1/2}$
17	Cl	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^5$		$^2P_{3/2}$
18	Ar	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6$		1S_0
19	K	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6$	$4s$	$^2S_{1/2}$
20	Ca	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6$	$4s^2$	1S_0
21	Sc	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d$	$4s^2$	$^2D_{3/2}$
22	Ti	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^2$	$4s^2$	3F_2
23	V	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^3$	$4s^2$	$^4F_{3/2}$
24	Cr	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^5$	$4s$	7S_5
25	Mn	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^5$	$4s^2$	$^6S_{5/2}$
29	Cu	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^{10}$	$4s$	$^2S_{1/2}$
30	Zn	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^{10}$	$4s^2$	1S_0
31	Ga	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^{10}$	$4s^2 \ 4p$	$^2P_{1/2}$
32	Ge	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^{10}$	$4s^2 \ 4p^2$	3P_0
33	As	$1s^2$	$2s^2 \ 2p^6$	$3s^2 \ 3p^6 \ 3d^{10}$	$4s^2 \ 4p^3$	$^4S_{1/2}$

definite rules concerning intensity of component groups of term lines. In those elements showing higher multiplicities than doublets, there are always two multiplicities, i.e., 1 and 3, 2 and 4, 3 and 5, etc., so that the spectrum may be further complicated by transitions from terms in one multiplicity to terms in another in what might be called intersystemal lines. These intersystemal lines are also governed by definite rules, such as the limitation of a change of L to 0 or ± 1 and a change of J to 0 or ± 1 . It is also impossible to have a change of state where $J = 0$ in both terms.

Only about half of the lines of the calcium spectrum are accounted for by the triplet-singlet systems together with their intersystemal jumps. The remaining lines are due to the simultaneous jumps of two or more electrons and the complete removal of one electron to yield a singly ionized calcium ion, which has an electron structure similar to that of

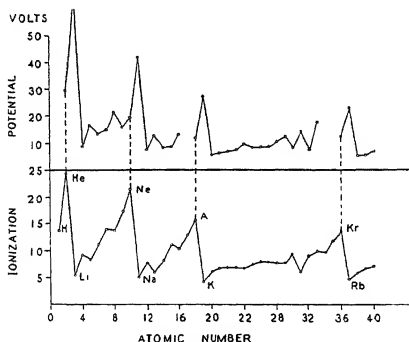


FIG. 2.8.—Ionization potential of some of the elements (I) (lower) and ionization potential of these singly ionized elements to doubly ionized elements (II) (upper). Note, in II series, that zero voltage for each element is its single-ionization potential.

the alkali metals, and hence will produce a doublet system. Further ionization can take place with the removal of additional electrons as a result of higher excitation potentials or temperatures. Many of these higher states of ionization are not available in our present laboratory methods, but are often observed in the spectra of stellar bodies. An example of the similarity between series of spectral lines produced by atoms with the same number of electrons but different proton or nuclear charge is shown in Fig. 2.7 (after Candler). The use of numbers I, II, III, and IV after the element symbol indicates the spectra of atoms which

contain all their electrons (I), have lost one electron (II), have lost two electrons (III), and have lost three electrons (IV). A succeeding greater voltage energy is required to produce a higher degree of ionization. Since the outer shell is the only part in which the atoms differ from each other in this assignment of electronic configuration, it is only necessary to indicate the last two terms to specify the atom. For example, Cl may be indicated as $3s^2 3p^5$ with a normal state of $^2P_{3/2}$ (Table 2.4). The necessity for the use of the last two terms rather than the final term is due to such an anomaly as is shown in K and Ca in which the $4s$ shell is completed before the $3d$, and in the long periods in the periodic table in which the higher s and lower d shells vary in the number of electrons. In the rare earths the $4f$ electrons in the N shell vary in number from 2 to 14, while the other shells, including the outer $5d$ and $6s^2$ shells, remain constant.

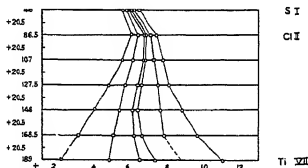


FIG. 2.9a.—Displaced frequency diagram in the sulfur I sequence showing regular frequency change in the $3s^2 3p^4 3P - 3s 3p^5 3P^o$ multiplet (Kruger and Pattin [C73]).

From this discussion of electron configuration it can easily be seen that the loss of an electron by ionization immediately changes the electron configuration to the preceding element in the periodic table, and, in a like manner, the normal state for this ionized atom and its multiplicity will follow the preceding assignment. Be I, with an outer electron configuration of $2s^2$ and normal state 1S_0 , on ionization to Be II conforms to the Li electron configuration of $2s$ with a normal state of $^2S_{1/2}$. The critical potentials for changes from state I to the ionized state II of the elements are indicated in Fig. 2.7. It will be noted that the inert gases have a maximum, indicating that considerable energy is required to destroy the completed outer octet shell, while the alkali metals with but one electron in the outer shell are the easiest to ionize. The ionization potentials of the singly ionized elements (II) to the doubly ionized states (III) indicate again the stability of the octet shell and the ease of liberation of the s electrons (Figs. 2.8 and 2.9).

Space limitations prevent the discussion of the anomalous behavior of many elements. The system of spectrum formation which has been

described in the preceding pages is not always followed with exactness, and there are many cases of inversion, quantum defects, series perturbations, and autoionization. The spectral analysis method for isotopes by

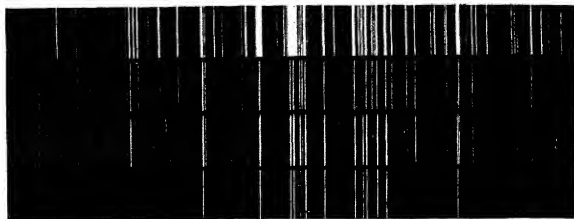


Fig. 2.9b.—Spectrogram of titanium (4300 Å region) in arc (top) and furnace at 2600°, 2300°, and 2000° (Carnegie Institution of Washington, Mount Wilson Observatory). Note change in relative line intensities with variation of excitation. P.

means of atomic spectra is difficult, and the theory involved in the explanation is too complicated to be adequately discussed in an analytical textbook (see section on band spectra).

BAND SPECTRA (DIATOMIC)

The most widely observed band spectrum and one which causes considerable worry to the analytical chemist is the CN band system produced



Fig. 2.10a.—CN bands (taken with a logarithmic sector to show relative intensity). N.

in a carbon arc in air (Fig. 2.10a). In the study of a band spectrum we are dealing with the excitation of a molecule rather than a single atom, and the mathematical analysis becomes much more difficult than for an excited atom involving but a single central proton or nucleus. With two or more nuclei within the excited body there will be inner vibrational, rotational, and electronic effects which will lead to variations from the single proton type, and because of the quantum effects these deviations will appear as regularly ordered satellite or band series. For purpose of nomenclature of the effects observed the symbols Σ , Π , Δ , and Φ are used

in place of the S , P , D , and F terms of the atomic spectra system. The electron configuration is expressed in much the same manner (Table 2.6).

TABLE 2.6

Atoms					Molecules						
C	1s ²	2s ²	2p ²	3P ₀ }	CO	1s ²	2p ²	2s ²	3p ²	2p ²	3d ² 1Σ
O	1s ²	2s ²	2p ⁴	3P ₂ }							

On account of this increased complexity in spectrum analysis, practically all the work that has been done has been confined to diatomic molecules. The same general rules can be applied in the analysis of band

FIG. 2.10b.—CaF bands at 5145 Å, (1,0) $^2\Sigma \rightarrow ^2\Sigma$. P.

spectra from diatomic molecules as have already been applied to the monoatomic spectrum analysis. An atom or molecule can emit only discrete amounts of energy corresponding to certain states or energy levels, and this energy can be related to the frequency of the emitted or absorbed radiation by the Bohr equation:

$$h\nu = E_1 - E_2$$

where E_1 and E_2 are the energy values of the two states or energy levels; h , Planck's constant; and ν , the frequency of the absorbed or emitted radiation.

ELECTRONIC, VIBRATIONAL AND ROTATIONAL ENERGY

As in the atomic spectrum, emission corresponds to a transition from a higher to a lower energy state, and absorption to the electron transition from a lower to a higher state. This energy value which represents the difference between the two states may be further resolved, in the case of molecules, into three factors which are known as electronic, vibrational, and rotational energy.

$$E = E_e + E_v + E_r$$

The electronic energy, E_e , is similar to the energy of the simple atomic spectra, and involves the two nuclei as a whole, especially with regard to the electrons on the outside of the molecule. The vibrational energy, E_v , is that produced from the vibration of two atoms along a line connecting them and can be defined by a single quantum number ($v = 0, 1, 2, 3, \dots$). The rotational energy, E_r , involves the energy of rotation about

the center of mass of the molecule and is defined by a group of quantum numbers including the quantum number J which determines angular momentum. A qualitative representation of this system is shown in Fig. 2.11 in which $^1\Sigma$ and $^1\Pi$ represent electronic levels (corresponding to S and P levels of atomic spectra). The dotted lines represent ground states in the two levels, Σ and Π , while

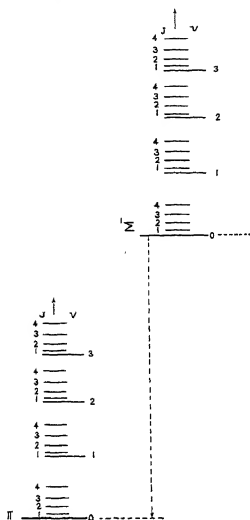


FIG. 2.11.—Energy levels in the $\Sigma \rightarrow \Pi$ band. Σ and Π indicate electronic states; $V=0, 2, 3, 4, 5$, etc., indicate vibrational and $J=0, 1, 2, 3, 4$, etc., indicate rotational states.

the quantum numbers v represent the vibrational levels, and the quantum numbers J represent the rotational levels. In magnitude the electronic values are large and correspond closely to atomic effects. The vibrational effects are quite small as compared with the electronic, and the rotational are still smaller. Electronic bands are produced when there is a change from one electronic level to another, i.e., when v_e is not equal to zero such bands involve vibrational, rotational, and electronic effects. When v_e is equal to zero the band systems produced are limited to vibrational and rotational effects, and here, if the vibrational energy change is not equal to zero, both effects may be involved. In any case the energy change is small and the bands will be limited to the near infrared. If the vibrational energy change is zero, then the only possible effects are in changes in the quantum number J , which will result in a series of bands in the extreme infrared due to the very low energy change. In general, the vibrational bands will increase in separation with lower quantum

numbers whereas rotational bands will decrease with lower quantum numbers. In vibrational bands two branches are found: R , the positive branch, where J increases by 1; and P , the negative branch, where J decreases by 1. The lines are thus indicated as $R(4)$ to show a transition of J from 5 to 4 in emission and the opposite transition in absorption. The band origin line ($P(0)$) is a missing line but can be easily determined by extension of the P and R curves. A third type of band branch is the Q

ISOTOPE EFFECT

branch which occurs in electronic bands where the J value is unchanged in the transition. $J' = J''$ (Fig. 2.12). The direction of degrading will depend upon the relative energy values of the different levels.

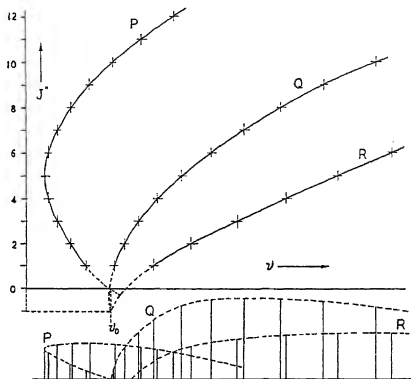


FIG. 2.12.—Fortrat diagram of the $\Sigma^+ - \Pi$ band of CO. P values correspond to electron shifts from nJ levels in Σ to $n+1$ levels in Π or a change of $+1$ in J . Q values correspond to a zero change in J and R to a -1 change in J . All P , Q , and R values in this diagram originate in the same level in Π and terminate in the same ν level in Σ . If the ν level in Σ is 0 and in Π is 0 the band is known as the 0, 0 band, and correspondingly if the electron shifts are from $\nu = 1$ in Σ to $\nu = 0$ in Π it will be known as the 1, 0 band.

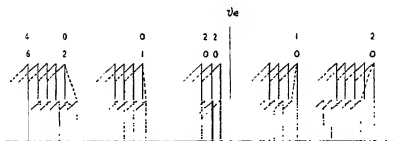


FIG. 2.13.—Isotope displacement in band spectra.

ISOTOPE EFFECT

Of particular interest to the chemist is the application of diatomic band spectra to the identification of isotopes. While electronic level displacement alone does not show appreciable differences, the added vibrational energy will cause a marked shift since the vibrational band is associated with vibrations whose energy depends on the actual masses

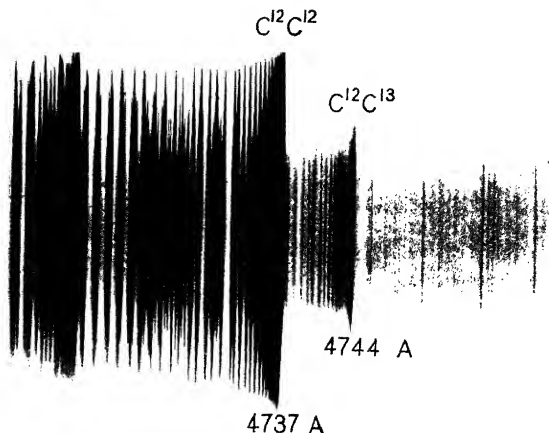


FIG. 2.14.—Isotope effect of C^{13} in the C_2 band spectrum (Birge and King). N.

of the two nuclei. Band structure in the stronger of the isotopic members will, however, often mask the presence of a weaker isotope band series unless the band head of the less abundant molecule lies outside that of the more abundant molecule (Figs. 2.13 and 2.14). Though not included within the scope of this book, it can at least be mentioned that the spectral studies of diatomic molecules can be applied to the determination of numerous important physical constants such as the heat of dissociation, ionization potentials, predissociation effects, and isotope concentration.

LITERATURE

General

"Elements of Atomic Spectrum Theory." A. C. Candler (*A7*).

"Atomic Spectra." Vols. I and II, A. C. Candler (*A6*).

"Spectra." R. C. Johnson (*A39*).

"Atomic Spectra and Atomic Structure." G. Herzberg (*A29*).

Reference

White (*A77*), Baly (*A3*), Jevons (*A38*), Scheibe (*A59*), Grottrian (*A31*), Kronig (*A44*), Glasstone (*A20*), Sommerfeld (*A65*).

CHAPTER III

EMISSION SPECTRA (APPARATUS)

SPECTROSCOPES AND SPECTROGRAPHS

The spectroscope has been developed from the observation of Newton in 1666 that white light in passing through a prism was dispersed into a spectrum. (By spectrum is meant the ordered arrangement of radiation in accordance with its frequency or wavelength.) Newton did not use a narrow slit for his illumination source, and so it remained for Wollaston and Fraunhofer (1802–1817) to make the observation that light sources such as the sun were not homogeneous, but involved light and dark spectral regions. Fraunhofer measured carefully the dark lines in the sun spectrum and indicated the more important lines by letters (Fig. 4.1*a*). This system of nomenclature is still used for these lines, such as the D, or yellow, sodium line. (See Frontispiece Plate I.) These dark lines in the sun spectrum are due to absorption of continuous radiation by vapors of the elements. By the comparison of the angle of bending of the light path

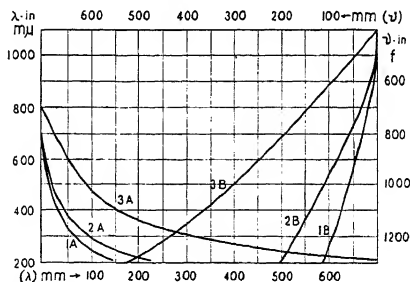


FIG. 3.1.—Dispersion curve for quartz spectrographs; *A*, against wavelength scale; *B*, against frequency scale. 1. Small Littrow (30 cm). 2. Medium Cornu (70 cm). 3. Large Littrow (180 cm).

with the wavelength of the light, we can establish a dispersion curve for the refracting substance. From the dispersion curve (Fig. 3.1) it can be seen that the separation is not linear, and hence, in the use of such materials as glass and quartz, it will be necessary to bend the photographic

plate to approximately the same curvature to record the spectrum at proper focus. This change in dispersion rate and focal point can be made more linear by the use of a compound lens system in what is known as the focusing lens of the instrument.

Fraunhofer first applied the principles of diffraction of light from a ruled grating (his grating was made of fine silver wires) to the measure-

ment of dispersion angles, and, by reason of the linear dispersion obtained in a grating, was able to assign actual wavelength values to the lines which he had identified in the sun absorption spectrum. Both these meth-

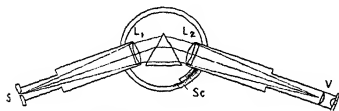


FIG. 3.2a.—Bunsen spectroscope.

ods of light dispersion have been employed in subsequent spectroscopic investigations, and the choice of a dispersion system in present-day spectroscopic studies is still largely a matter of personal preference, availability, and cost.

The simple spectroscope as devised by Bunsen (Fig. 3.2) involves a slit (*S*), collimating lens (*L*₁), refracting prism (a 60° prism of quartz, glass, or other refracting medium), a focusing lens (*L*₂), and an eyepiece (*V*). Through this eyepiece it is possible to examine the spectrum so long as it remains within the visible range. For extension beyond the visible, the recording of the complete spectrum; and the study of faint lines whose intensity is not sufficient to produce a visual effect, but whose integrated intensity over a period of time would be sufficient to produce a photographic effect, a modification of the spectroscope has been devised, namely, the spectrograph (Fig. 3.3), which utilizes a photographic emulsion for the recording of the spectrum. Because the lens systems involve the principle of refraction of light, as a means of focusing, and the physical phenomena of dispersion, upon which the whole spectrographic



FIG. 3.2b.—Spectroscope, telescope tube in front, collimator tube and slit on the right, scale illuminating tube left (rear) (Gaertner).

principle is based, it is apparent that the focal length of a simple lens or system will be shorter for those rays which are bent at a greater

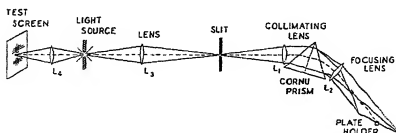


FIG. 3.3.—Optical diagram of a spectrograph.

We may, therefore, expect a change in focal length and dispersion rate on the photographic plate which will approximate the dispersion curve of the refracting medium (Fig. 3.1).

A partial correction of the necessary curvature of a photographic plate may be made by means of a suitably selected set of lens components in

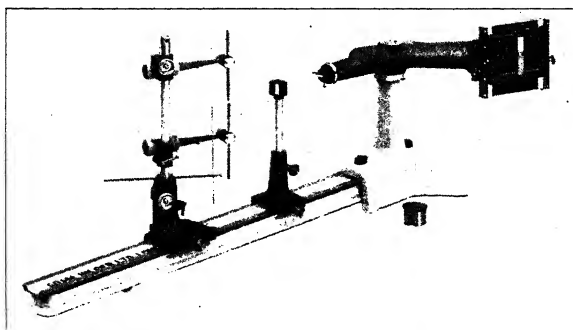


FIG. 3.4a.—Hilger spectrograph, 20 cm (small).

Note: In order to indicate spectrograph sizes, in this book the following notations of small, intermediate, medium, large (sometimes indicated as Littrow, without designation of size), and extra large are used:

Designation	Focal length (F_D)	Spectrum length	Negative size
Small.....	20 cm	2000–8000 Å	4 1/4 inch
Intermediate.....	40	14	7 inch
Medium.....	60–75	22–25	10 inch
Large.....	150–180	60–80	10 inch (3×)
Extra large.....	300	120	10 inch (6×)

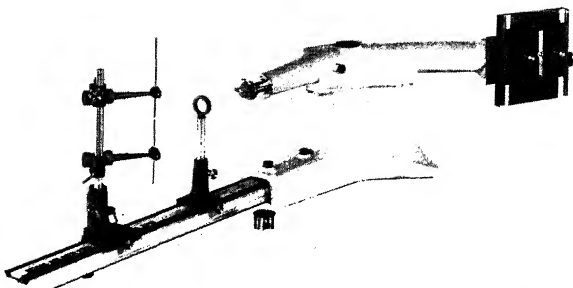


FIG. 3.4b.—Hilger spectrograph, 38 cm (intermediate).

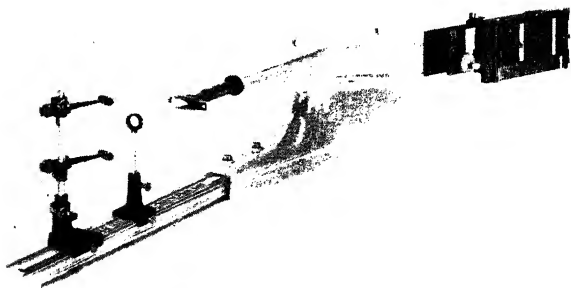


FIG. 3.4c.—Hilger spectrograph, 60 cm (medium).

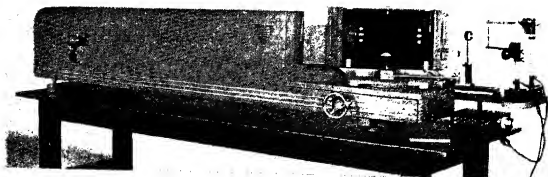


FIG. 3.4d.—Bausch and Lomb spectrograph, 180 cm (Littrow).

the focusing lens, just as one may correct the focal points of a photographic lens, so that various wavelengths of light will have the same focal point, in what is known as an achromatic lens. In this correction

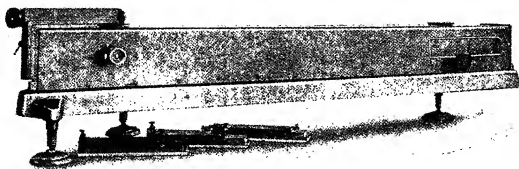


FIG. 3.4e.—Gaertner spectrograph, 170 cm (Littrow).

no attempt is made to alter the slope of the plate with regard to the normal beam from the prism, but rather to reduce the curvature of this focal plane so as to avoid too severe a bending of the photographic plate. Even with this applied correction it is often necessary to use very thin glass plates or film base for the photographic emulsion rather than the usual photographic plate which could not stand the bending strain.

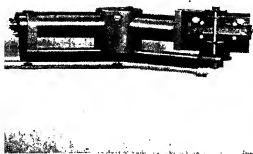


FIG. 3.4f. Zeiss spectrograph 60 cm (medium).



FIG. 3.5.—Lens and prism assembly (medium Bausch and Lomb spectrograph).

The spectroscope or spectrograph is most efficient when the incident and refracted beam form the same angle with the prism—the angle of minimum deviation. Most spectrographs are so constructed that this angle is formed between the middle of the spectrum plate and the prism

face, and the slit and the prism face (Fig. 3.3). The object of the collimating lens (L_1) is to bring the light into a parallel beam as it passes through the prism (P) and thus cause the beam to strike the prism at a uniform angle so as to produce the same dispersion, at any wavelength, for all parts of the beam. The focusing lens (L_2), as has been mentioned, brings the parallel dispersed beams into focus on the photographic negative placed at the focal plane.

PRISMS

Certain modifications of the simple instrument described above have been developed, among which the Littrow spectrograph is outstanding in importance. In this modification (Fig. 3.6), advantage is taken of the

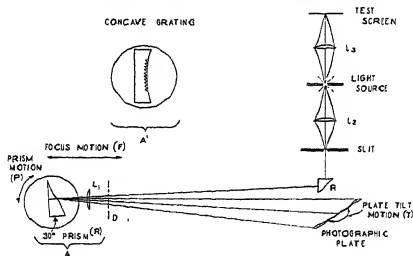


Fig. 3.6.—Diagram of Littrow spectrograph (see Exercise 3, Chapter XII for a description of parts and adjustment).

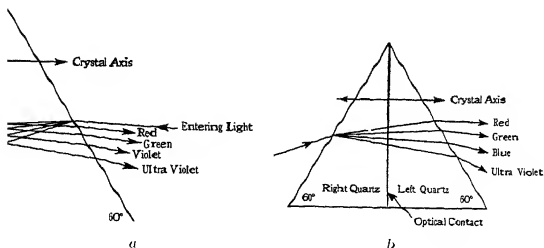


Fig. 3.7.—Littrow (*a*) and Cornu (*b*) prisms (Bausch and Lomb).

use of a 30° prism with a mirror-back face so that the beam of light passes through the prism to the mirror face and is reflected back through the prism, the total path being equivalent to a 60° prism (Fig. 3.7*a*). In the

use of certain natural products, such as quartz crystals, as the refracting medium, the nature of the crystal structure is such as to require the cutting of the refracting prism along certain definite optical axes, and, except for that light which is refracted at exactly the angle of minimum deviation, there will be a doubling of the image due to the optical properties of quartz. To correct for this, Cornu has devised a prism which bears his name (Fig. 3.7*b*), in which the 60° prism consists of two halves of 30° each in optical contact and composed of quartz of opposite rotatory

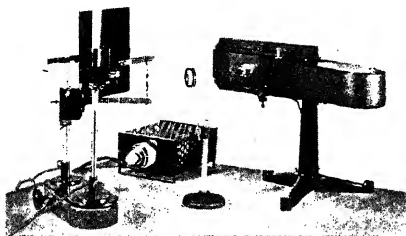


FIG. 3.8.—Small Littrow (Bausch and Lomb) (30-cm focal length—210 to 700 15 cm).

power, i.e., one dextro and one levo prism: this results in a complete correction of the defect. In the Littrow modification it is not necessary to apply such a correction, as the reversal of the beam by the mirror surface

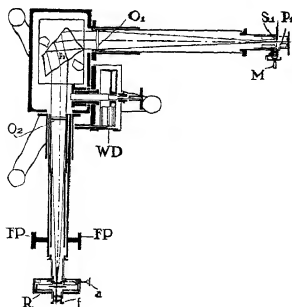


FIG. 3.9*a*.—(left) Diagram of constant-deviation spectrometer. S_1 , slit; P_1 , constant-deviation prism; WD , wavelength drum; F , eyepiece.

FIG. 3.9*b*.—(above) Hand spectroscopy. O , collimating lens; S , slit; P , prism (Bausch and Lomb).

and the return of the beam through the same prism results in a correction of this doubling effect (Fig. 3.8).

Among the other modified prism instruments are constant-angle and direct-vision spectroscopes and spectrometers (Fig. 3.9). A spectrometer

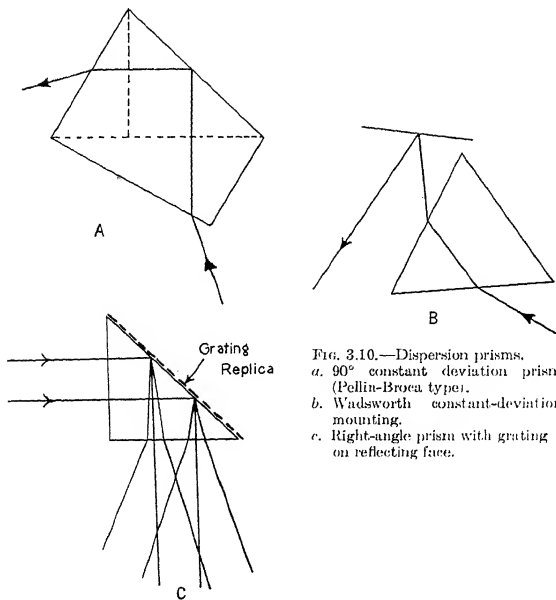


FIG. 3.10.—Dispersion prisms.
a. 90° constant deviation prism (Pellin-Broca type).
b. Wadsworth constant-deviation mounting.
c. Right-angle prism with grating on reflecting face.

supplies light of a constant frequency from a homogeneous source and may be considered an instrument for measuring the frequency or wavelength of the observed heterogeneous source. Two constant-deviation prisms are shown in Fig. 3.10, in which the refracted beam is reflected either by a right-angle prism (*A*) or a plain mirror (Wadsworth mounting) (*B*). The result of this reflection is to reverse the spectral order so that a constant angle is obtained for all wavelengths at the angle of minimum deviation of the prism.

GRATINGS

On account of the scarcity of ruled gratings it has been difficult to obtain satisfactory ones for medium-sized instruments such as would be used by the chemist. With the recent development by Wood of a rapid and accurate method of ruling on glass and aluminum, and the ability to aluminize glass gratings, it is apparent that this form of dispersion for spectrographs will be used to a much greater extent in the future. Of the various methods of mounting a grating, the most generally ac-

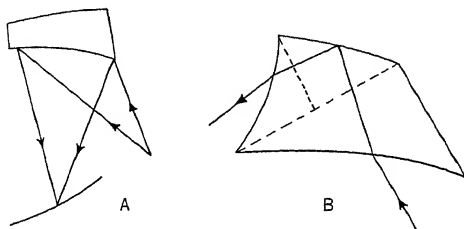


FIG. 3.11.—Combination lens and prism systems.
a. Féry. b. Caillier.

cepted form for the chemist is known as the Eagle mounting. This is quite similar to the Littrow mounting for a prism spectrograph, and, in fact, there are available on the market instruments with interchangeable grating and prism systems (Hilger—185) (Fig. 3.6.4'). The grating, in itself, is only a dispersion medium, and it is still necessary to use a collimating and focusing lens. As in the Littrow-mounted prism instrument, the same lens may function both as a collimating and focusing device. As a further simplification in both the Eagle-mounted grating and the Littrow-mounted prism instruments, a combination lens and dispersion piece has been devised. In the grating instrument this involves the use of a concave mirror as the lens system, upon whose surface is ruled the grating. Such a grating is generally called a concave grating, and because of the uniform reflection of light regardless of wavelength it acts as a fully corrected achromatic lens system. In the prism instrument the effect is produced by grinding both the front and back of the prism as two lens surfaces with an angle of 30° between the arcs formed by the two curved surfaces (Fig. 3.11.A). This prism, which is known as a Féry prism, while very economical of quartz is not extremely satisfactory on account of its inability to produce an achromatic lens effect.

Concave gratings, by reason of their optical principle, do not produce a spectrum of stigmatic character, and the image produced on the plate is not a photographic image of the slit but rather an integrated and redistributed image of the slit intensity. This prevents the use of a step sector or slit diaphragm at the slit, although a similar diaphragm has nearly equal effectiveness at the plate (Fig. 3.12).

The choice of dispersion medium is dependent in part on the spectral range to be covered. For the photographically sensitive region of the

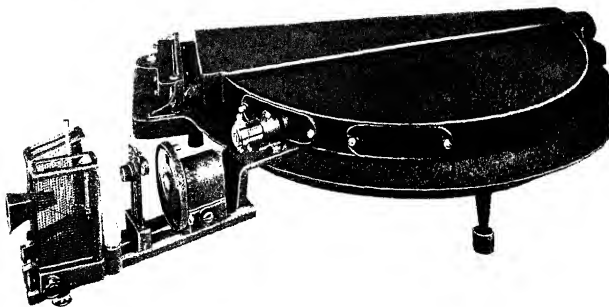


FIG. 3.12a.—Applied Research Laboratories grating spectrograph (H. W. Dietert Company).

ultraviolet, quartz is the most acceptable; for the near ultraviolet and visible, glass and gratings; and for the infrared, rock salt or sylvite crystals and gratings may be used.

SLITS

Since in most instruments the photographic image in the spectrogram (spectrum photograph) is a replica of the slit, and in all instruments the spectral purity is a function of the slit characteristics, it is quite essential that the slit of the instrument be of exceptionally fine quality (*A15*). So far as the spectroscope or spectrograph is concerned, the slit is the light source from which the spectrum is obtained. An auxiliary light source from without is of course used to illuminate the slit, but the actual photograph obtained is a reproduction of the slit in each detail. If the slit has a slight indentation or projection caused by a nick in the jaw edge of the slit, or a dust particle, then each spectral line will show this as a wide or narrow difference in the spectral-line width, and in the entire spectrogram the dust particle will appear as a white streak on the

negative, and the nick as a black streak. It is therefore quite essential that the slit be carefully cleaned to guard against the presence of dust

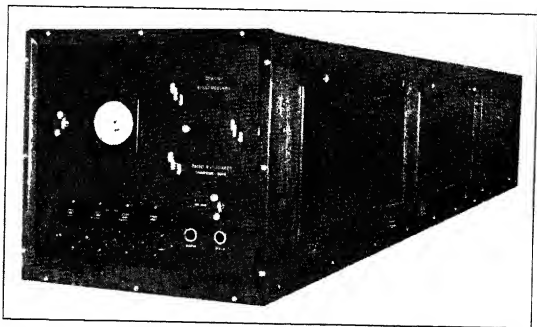


FIG. 3.12*b*.—Grating spectrograph (concave grating in Eagle mounting) (Baird Associates).

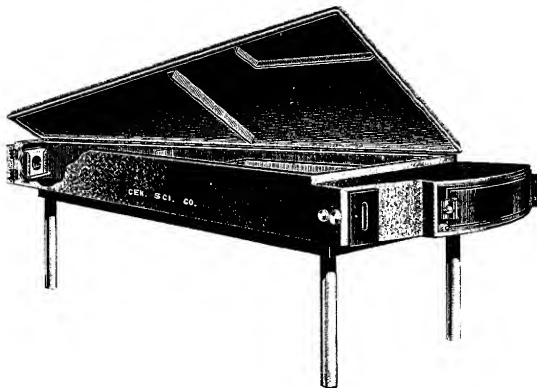


FIG. 3.12*c*.—Grating spectrograph (replica grating) (Central Scientific Company).

particles between the jaws of the slit at the time of closing, and that extreme care be taken to prevent damage by closing the slit beyond the point of contact of the two edges.

In certain instruments, such as the Bausch and Lomb, the screw motion to open the slit is set to operate against a spring which normally holds the jaws together, and which is blocked at the point of contact so that it is impossible to damage the slit by turning the adjustment screw beyond the zero slit opening. In general, spectrographic slits are produced by cutting some non-corroding metal with bevel knife edges so that the bevel surface is facing the prism, and the outer surface appears as a flat surface when the two jaws are in contact (Fig. 3.13).

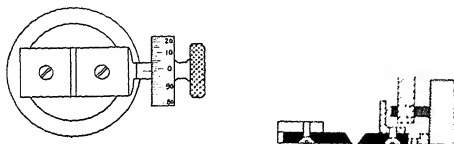


FIG. 3.13. -- Diagram of unilateral spectroscopic slit.

DIAPHRAGMS

Since, in all prism instruments and in certain optical modifications of the grating instruments, the spectrogram is a reproduction of the slit at different wavelength positions, the ideal place to introduce any diaphragms for superposition of one spectrum on top of another will be at the slit. Special diaphragms are available for the purpose (Fig. 3.14), by means of which one may vary the height of the spectrum on the plate.



FIG. 3.14. -- Hartmann diaphragm.

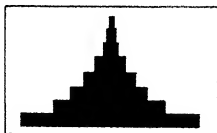


FIG. 3.15. -- Hanen step-slit.

and thus by motion of the plate, in a direction at right angles to the spectrum, record a number of separate spectrograms on the same negative. With the Hartmann diaphragm which involves a number of openings in echelon it is possible to record several spectrograms on the same negative without moving the plate holder. This avoids any lateral shift of the spectrogram due to motion of the plate holder, or to an error in

adjustment of the slit (i.e., if the slit is not parallel to the refracting edge of the prism, thus producing sloping lines in the spectrogram).

In some types of analysis (see discussion on quantitative analysis) it is desirable to have a series of photographs taken at different exposure periods. This can be approximated by the use of a step slit, in which the step edges of the slit act as diaphragms of different aperture (Fig. 3.15). Such a slit was designed by Hansen (C58) in 1924 and applied to a spectrograph, Duffendack (1934) (C44) has described this type of slit in a basic patent covering the principles of quantitative emission analysis.

A similar step slit for direct attachment on a spectrograph with slit steps of 0.02, 0.04, 0.08, 0.16, 0.32, 0.64, and 1.28 mm has been described by Scheffer in the catalogs of Franz Schmidt and Haensch (1912 and 1929). This type of slit (Fig. 8.12) enables the observer to compare a series of intensity measurements in a single photograph. The same effect can be obtained by placing a step sector in front of the slit, or by means of a graded density wedge such as can be produced by layers of evaporated aluminum of a varying thickness on quartz. It is to be noted that in the latter two methods the purity of the spectrum line remains constant, while in the step or wedge slit method there may be some error due to broadening of the line to include adjacent lines as well as a broadening rather than increase in density of the line after a certain density of image has been reached. In connection with the quartz plates with sputtered or evaporated density pattern it is of interest to call attention to quartz plates which have been silvered, and then a fine line of known width ruled or cut in the silver so as to produce a slit of known width. Such a slit can then be copper plated to yield a very practical slit of fixed width. Several such slits can be ruled on the same piece to provide a series of variable known slit widths. The slit on the Bausch and Lomb small Littrow spectrograph is an example of this. In large instruments this quartz plate may produce interference fringes on the lines, which can be partially eliminated by a sloping plate or a plate of a slightly wedge character.

CONSTANT-DEVIATION SPECTROMETERS

For visual inspection of emission spectra and a study of visual absorption spectra, one may use the simple Bunsen spectroscope or the more convenient constant-deviation spectrometers (Figs. 3.9*a* and 3.16). The usual constant-deviation spectrometer has a combination 30-90-30° prism (Fig. 3.10*A*), although some instruments are available in the Wadsworth mounting (Fig. 3.10*B*), or a right-angle prism and a grating replica (3.10*C*). In the usual visual spectrometer, the operating drum is graduated in millimicrons, and in most instruments a variable :

is provided in the eyepiece so that a considerable portion of the spectrum can be seen at one time, or the slit can be narrowed to the width of a single line. Because of stray light which may be a bother in making readings at the blue and red ends of the spectrum, many instruments have a built-in red and blue filter so as to cut out a considerable portion of the stray light.

Where an ultraviolet spectrometer or monochromator is desired in order to furnish a high intensity of monochromatic radiation, the usual

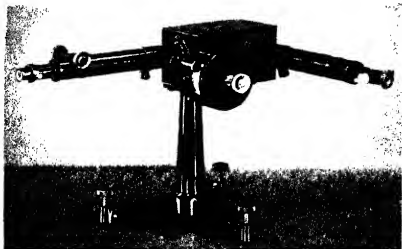


FIG. 3.16a.—Spectrometer (Bausch and Lomb).

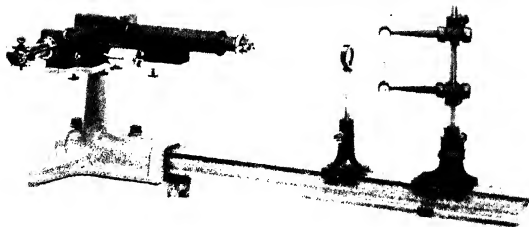


FIG. 3.16b.—Spectrometer (Hilger).

type of instrument employed for this purpose is the double prism type such as the van Cittert (Fig. 3.17), Bausch and Lomb (Fig. 3.18), Gaertner, or Hilger.

EFFICIENCY OF SPECTROGRAPHIC EQUIPMENT

The art of producing high-grade spectrographs of exacting precision requirements is such as seriously to limit the available sources of spec-

troscopes and spectrographic equipment. Since in most spectrographic laboratories the initial cost of the instrument is small when spread over the period of years of usefulness of the instrument, it is worth while to consider, in the purchase of an instrument, the quality and performance

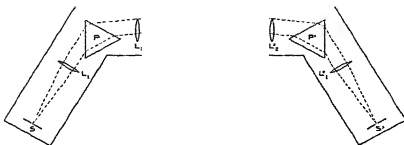


FIG. 3.17.—van Cittert double-prism quartz monochromator (Kipp and Zonen).

ability of the instrument in addition to any price considerations. It is often true that for some exacting spectroscopic studies an expensive instrument has in the end proved itself more economical than the lower-price instrument. On the other hand, there is a feeling in some laboratories



FIG. 3.18.—Monochromator (Bausch and Lomb).

that the best instrument for any particular purpose will be the most expensive. That this is not so can be seen by the comparison of the focal length and lens apertures of the small, medium, and large instruments of any manufacturer as compared with the price. It may be seen that the lens diameter of the 1.5-meter-focal-length Littrow instrument, which is a common size in many makers' instrument types, has a lens which is only slightly larger than the 75-cm Cornu type, which is also a

very common size. The latter yields a complete spectrum on a 10-in. plate; the former requires four 10-in. plates. The Littrow instrument has a considerably greater dispersion and only a slightly greater resolving power. Its effective aperture will, on the other hand, be smaller, and, for the examination of samples involving very minute traces of material, the smaller instrument of greater light-gathering power is to be preferred over the larger instrument of greater dispersion.

For absorption spectra measurements on all types of solutions, the medium-sized (75-cm-focal-length spectrograph mentioned above) should

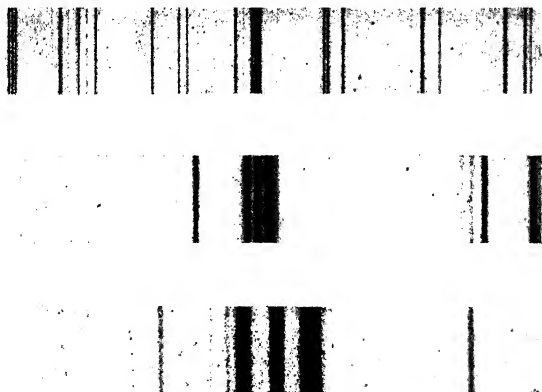


Fig. 3.19.—Photograph from small, medium, and large spectrograph, showing change in dispersion. N (iron triplet at 3100Å) (Higer).

be ample in size. For metallurgical studies on the elements of simple spectra, such as copper, brass, aluminum, zinc, and die-cast alloys, this instrument should also prove quite satisfactory. On the other hand, for studies of steel samples, for nickel, chromium, thorium, rare earths, and the like, a higher dispersion and resolution is almost necessary if one is to be able to separate the lines sufficiently for the identification and estimation of the amounts of impurities present.

DISPERSION (C134)

The efficiency of a spectrograph depends on a number of factors, chief among which is the dispersion and resolving power. The dispersion of

any instrument of the spectrometric type is defined as the ratio of the change in the deviation of the light beam ($d\theta$) to the change in wavelength ($d\lambda$) and is expressed by the mathematical form ($d\theta/d\lambda$). Dispersion is dependent on the refracting angle and the composition of the prism. The composition of the prism, rock salt, glass, quartz, or other material, influences the bending of the beam on account of the variation of the refractive index of the material as compared with the refractive index of air. One may therefore express the dispersion of a prism as a function of the angular bending (θ) and the variation of the refractive index (n) with a change of wavelength (λ) in accordance with the following equation:

$$\frac{d\theta}{d\lambda} = \frac{\delta\theta}{\delta n} \cdot \frac{\delta n}{\delta\lambda} \quad (1)$$

The ratio of the change of deviation with a change of refractive index can be expressed for a 60° prism as

$$\frac{\delta\theta}{\delta n} = \frac{1}{\sqrt{1 - \frac{n^2}{4}}} \quad (2)$$

The remaining part of equation (1) can be determined from the Hartmann formula

$$\lambda = \lambda_0 + \frac{c}{(n - n_0)}$$

and can be expressed as

$$\frac{\delta n}{\delta\lambda} = - \frac{c}{(\lambda - \lambda_0)^2} \quad (3)$$

Substitution of equations (2) and (3) in equation (1) will give the expression

$$\frac{d\theta}{d\lambda} = \left(\frac{1}{\sqrt{1 - \frac{n^2}{4}}} \right) \left(- \frac{c}{(\lambda - \lambda_0)^2} \right) \quad (4)$$

The values of c , λ , λ_0 , and n_0 can be determined if the refractive indices for three points are known. The final expression signifies a certain angular separation for any pair of lines of known wavelength separation and is independent of the size of the prism or spectrograph.

RESOLVING POWER

The resolving power of a spectroscopic instrument is the ratio between the average wavelength of a pair of lines that can just be separated, and the difference in wavelength between these two lines:

$$R = \frac{\lambda}{\Delta\lambda}$$

For example, in an instrument which could just separate the two sodium lines in the D pair this expression would become

$$R = \frac{5893}{5896 - 5890}$$

It can be shown that

where t is the base of the prism, and hence, where the refractive index wavelength change remains fairly constant, as it does with most prisms, the resolution will depend on the prism size and will be independent of the focal length or magnification of the final negative. The practical resolving power of a spectroscope is always much less than the theoretical resolving power (R) since this latter value is dependent on lines and slits of extremely narrow finite width. In practice, the following relations hold with respect to the slit width, purity (practical resolving power), and intensity. The normal slit (slit factor = 1.0) is defined as the width for which the extreme difference from one edge of the slit to the nearest and farthest edges of the collimating lens is $(\lambda/8)$, or as expressed in millimeters by multiplying by the factor $f\lambda/4D$, where f is the focal length in millimeters, λ the wavelength, and D the effective diameter of the lens. The normal slit gives a purity of spectrum (approach to theoretical resolving power) which is 1.4 per cent less than the maximum possible. If the slit factor is increased to 2.0, nearly double the amount of light is transmitted by the slit and the purity drops to 5.7 per cent below the maximum. A gain of three times the light means a loss of about 20 per cent of the purity, while a slit factor of 3.67 means a loss of half of the resolving power, and further increase in width decreases the purity or resolving power without much gain in intensity.

LIGHT SOURCES

Atoms and molecules are excited by application of energy in the form of heat or electricity. Low-temperature excitation is best obtained by a flame, producing temperatures from 1000 to 3000° C. For higher temperatures electric arcs may be used, in which temperatures from 3000 to 6000° C may be obtained, and for still higher temperatures a spark source may be used. For gaseous materials an electric discharge (Geissler tube) forms the most convenient means of excitation.

Flame Sources. Excepting for the alkali metals the flame source is not a very satisfactory method of atomic excitation. The qualitative flame testing of unknowns is, however, important, and the use of a dark purple glass for the test of potassium in the presence of sodium is essentially a spectrometric examination in which the colored glass acts as the disper-

sion instrument. To avoid a continuous background one needs a nearly colorless flame into which the sample may be introduced, either externally, by means of a platinum wire, asbestos-soaked piece, or spray; or internally, by means of an atomizer system in the gas or air line so as to pass a spray into the flame, or volatile compounds of the element to be tested (Fig. 3.20). The determination of boron by means of methyl borate is an example of this last method, namely, the introduction of a volatile compound into the flame.

The disadvantage of a flame source lies in its relatively low temperature, and hence its ability to excite only the alkali metals and the lower states of the alkaline earths and a few other elements. This disadvantage becomes an advantage where it is desired to detect these substances in the presence of a large amount of material of higher excitation potential.

With the alkaline earths and a large number of other substances, the spectra produced will consist largely of diatomic or molecular band spectra rather than the atomic line spectra. Copper, in itself, does not color the ordinary flame but the halogen salts of copper impart a brilliant green to the flame color with the production of a band spectrum of the corresponding copper halide.

At ordinary flame temperatures the red color produced on the heating of strontium nitrate is not due so much to excited strontium as to the band spectrum of strontium oxide, and the same is true for the calcium and barium flame colors. The flame tests are usually made with the halides, owing to the lower volatility and excitation potentials of these salts, and identification is often made from a band spectrum rather than a line spectrum. The flame tests may also be utilized to identify certain anions such as the halogens, which can be identified only with great difficulty by the higher excitation methods of atomic spectra.

Arc Sources. Probably the most widely used and most satisfactory method of atomic excitation is the electric arc. Temperatures in the electric arc range from 1000 to 6000° C., depending on the current density and electrode size (Fig. 3.21). The electric arc is a polarized source, and hence one would expect a high concentration of negatively charged particles in the neighborhood of the positive pole and of positively charged particles in the neighborhood of the negative pole. Some metals, such as iron, tend to form a bead of oxide at the positive pole (cathode) so that it should be the lower electrode in the direct-current arc. For other metals the polarity may not be of great importance, and either polarity may be used for the bottom electrode.

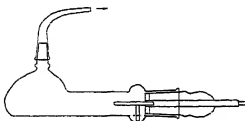


FIG. 3.20.—Lundegardh atomizer for flame spectra of salt solutions (452).

For most spectroscopic determinations it is not desirable to use the entire arc as a source but rather to focus on the center of the arc, so as to avoid the ionic concentrations at the poles and the continuous spectrum produced by the incandescent pole pieces. For simple spectrum photographs this can be accomplished by focusing the entire image of the arc on the spectrum slit, so that the image is about two to three times the length of the desired slit height, and inserting a wedge or Hartmann diaphragm in front of the slit to cut off the unwanted ends of the arc image. For purposes of alignment in both arc and spark apparatus it is advisable to have an optical bench with fixed electrode positions, and a

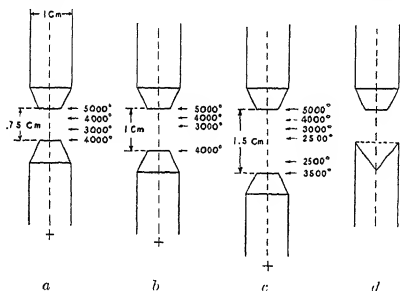


FIG. 3.21.—Relation between gap length and relative temperatures in a carbon arc (a, b, c).

Cupped carbon for analysis sample (d).

secondary lens system (L_4) to focus the source on a test screen (Fig. 3.3). The purpose of the secondary lens and screen is to permit a rapid adjustment and alignment of the arc or spark source, since the optical path of the spectrograph and light source may be set in line with the secondary lens and screen. Numerous types of arc and spark holders are available on the market, between which there is little difference in regard to method of use (Figs. 3.22 and 3.23). Most arc holders are sufficiently well insulated thermally and electrically to be used for either arc or spark determinations. The ideal arc holder should be independently adjustable in a direction parallel with the slit and perpendicular to the optical path, and perpendicular to the slit and perpendicular to the optical path. It should be adjustable in a direction parallel with the optical path, although this is not essential, and any such desired adjustment could be made by a change in the focal position of the lens (L_1). For the production of a mixed spectrum from two different materials, such as nickel and

iron, it is essential to set the electrodes in a horizontal position (perpendicular to the slit) rather than parallel with the slit. Such an adjustment is provided in the arc holder illustrated in Fig. 3.22. The arc holders should be capable of taking $\frac{1}{4}$ - to $\frac{3}{8}$ -inch rods directly, as well as smaller rods or wires, and, in addition, spring clips should be available

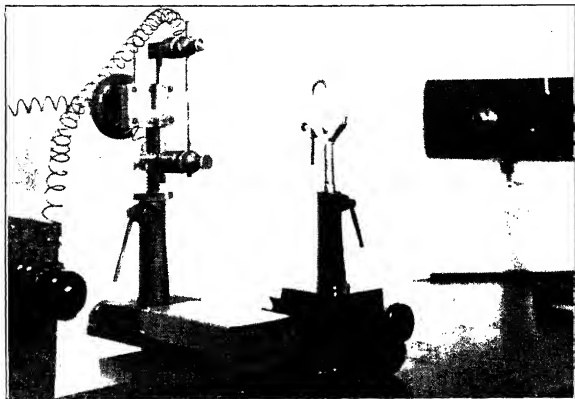


FIG. 3.22.—Arc and spark electrode holder on optical bench. Arc holder has been reversed on optical bench to show construction. Both lens holder and arc holder have a similar base with a locking screw to clamp to optical bench (lower disk) and a side-wise motion screw (upper disk). Arc holder has a vertical motion ring adjustment (above locking lever). The threaded shaft has a keyed slot to keep arc in alignment. An insulated knob operates a rack and pinion adjustment of arc or spark width. Electrode clamps are insulated for spark use and constructed with cooling fins for arc use. Material may be used in rod form or held by spring clips.

for these holders so as to permit the use of small or irregularly shaped samples.

Carbon Electrodes. For nonmetallic-nonconducting samples it is necessary to have a conducting electrode such as carbon and to introduce the sample in small pieces or powder form into a cored portion of the lower (positive) electrode. For such analyses the carbon electrode need not be over an inch long, and the cored recess, which can be produced by a machine drill, should be about 4 or 5 mm deep (Fig. 3.21d). It is recommended that solid electrodes greater than $\frac{1}{4}$ inch should not be used for arc measurements unless a high current density is also essential. Good

EMISSION SPECTRA (APPARATUS)

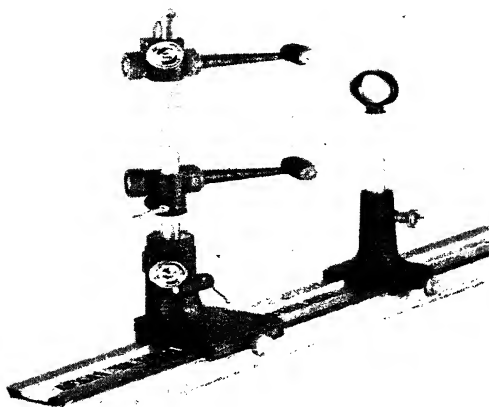


FIG. 3.23*a*.—Arc and spark holders (Hilger).

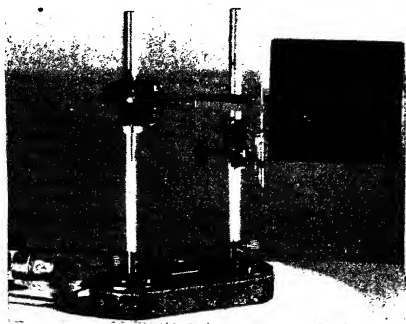


FIG. 3.23*b*.—Arc and spark holders (Bausch and Lomb).

carbon electrodes, free from nearly all impurity elements, can be obtained from the National Carbon Company. These are known as Acheson spectroscopic carbons. A still purer form of carbon electrode can be obtained from the same company, from the Dow Chemical Company, or from the Speer Company. These high-purity carbon electrodes are free from even spectroscopic traces of most impurity elements. This extra degree of purification increases the cost of the electrode (1 inch by $\frac{1}{4}$ inch) from about one cent to about ten cents (assuming that a number of 12-inch rods are purchased by the user at one time and cut to the inch size), but it is often worth the added cost when the elements under investigation may be impurity elements in the spectroscopic carbons. For many purposes, however, the lower-priced electrodes will be found to be quite satisfactory.

Arc Spectra of Solutions. Special technique may be necessary in the examination of the arc or spark spectrum of solutions. In the examination of solutions, it has been suggested that the solution be allowed to drop slowly into a cored receptacle of a hot (about 105° C) electrode (*C100*). After evaporation the electrode may be arched in the usual manner. If there seems to be a tendency for the liquid to diffuse through the electrode instead of evaporating in the cup, a drop of kerosene may be introduced into the cup before the above evaporation procedure in order to reduce the penetration into the electrode of the aqueous solution.

Heterogeneous Samples. If the sample to be examined is a heterogeneous material, such as a composite mixture of turnings from a large number of pieces, in which an average analysis is desired, it may be necessary to use a larger sample holder, such as a metal plate or cup, and to burn the arc for some time to obtain an average sample (*C19*). In such cases the light intensity can be reduced on the slit by means of a diaphragm at the focusing lens or by the entire elimination of a focusing lens between the arc and slit. In place of a diaphragm, absorbing wire screens or a rotating sector may be used to allow greater sampling from the arc with a given photographic exposure. In most spectrographs, diaphragms are also provided at the lens (L_1) adjacent to the prism (focusing lens), and these will have the same effect on the photographic intensity as diaphragming the slit lens.

Shutter Mechanism. In the preliminary adjustment of the light source it is desirable to be able to focus on the slit and observe the arc position with regard to the slit opening, before any exposure has been made. For this reason it is essential that the instrument be equipped with a shutter mechanism between the slit and the plate. (The use of the dark slide of the plate holder for this purpose is unsatisfactory in that it requires

considerable manipulation and may result in a lateral motion of the plate between spectrum photographs.)

Electrical Circuit. The electrical circuit for an arc source is indicated in Fig. 3.24. It is assumed that there is available a d-c supply of at least 110 volts, and a higher voltage is often of some advantage since it will permit an easier control. The electrical circuit should have an ammeter in series with the supply, and a voltmeter attached to the leads to the electrodes so as to record the voltage drop across the electrodes. A resistance (R) and inductance (L) should be included in the circuit. The

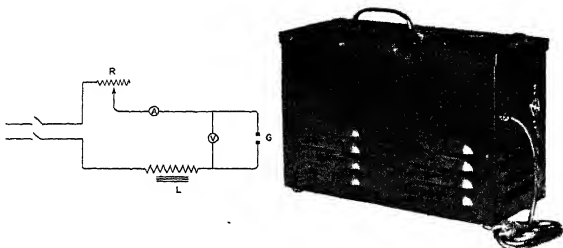


FIG. 3.24.—Electrical circuit for an arc source.

FIG. 3.25.—Rectifier for arc source, converts 115-volt alternating current to 60-volt 5-ampere direct current (Raytheon Manufacturing Company).

resistance should be of an adjustable slide-wire type and capable of carrying a load of 10 amperes at 12 ohms resistance. The inductance will steady the arc and maintain a more constant voltage. For most current supply, the primary of a 1-kva transformer, in which the secondary windings have been shorted, will act as a very satisfactory inductance.

In laboratories where direct current is not available through a battery, converter, or power supply, or where the arc would prove too much of a drain on the battery system, it is suggested that a portable rectifier (Fig. 3.25) be used. This special type of rectifier is designed for supplying current to a $\frac{1}{4}$ -inch electrode arc and is built with a current-limiting transformer so that an external ballast or inductance is not necessary. The model illustrated supplies 5 amperes at 60 volts direct current and operates from 115 volts alternating current.

Duffendack, Owens, Wolfe, and others have suggested the use of a high-voltage alternating current arc for spectroscopic illumination (*C17*) and have claimed many advantages in reduction of background, low heating effect of electrodes, and small sample requirements, as well as certain

excitation advantages resulting from the higher voltage. The use of this high-voltage (2000 volts) a-c arc involves some possible experimental hazard, and it is not advised for open classroom work. For industrial or routine analysis by competent observers there should be no great danger if proper precautions are maintained. The arc holder itself (Fig. 3.26)

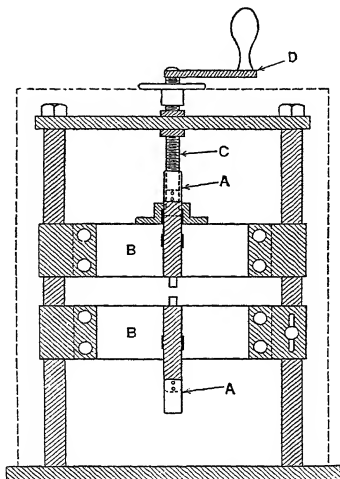


FIG. 3.26.—High voltage a-c arc holder. *A, A* are spring clamps for holding the electrodes; *B, B* are Bakelite insulators; and *C* is a screw of 0.5-mm pitch which may be turned by the insulated handle, *D*. The lower electrode can be adjusted in position by sliding it on the uprights, and the upper electrode is set by means of the screw. The arc stand is enclosed in a cage to protect the operator from the 2200-volt circuit which maintains the arc. (Duffendack and Wolfe [C45].)

has been designed for rapid analysis procedure with electrodes of uniform length which are inserted into the lower electrode so that the height of the electrode will always be at the center of the optical path. The top electrode is held in a screw and friction clamp so that it may be screwed down to contact with the lower electrode by means of the insulated handle. Continued screwing down on the handle will merely cause the electrode to slide in the friction part of its holder, but on reversing the screw motion the electrodes will immediately start to separate. Since the pitch of the screw is in millimeters, it is possible to screw the electrode

down to the sample electrode and continue until the handle reaches a given mark and then, reversing the direction to one half or one revolution, thus to produce a gap of $\frac{1}{2}$ or 1 mm. While in normal arc sources the gap will be from 5 to 10 mm or even greater, this type of a-c arc will be found to operate best at a gap width of $\frac{1}{2}$ to $1\frac{1}{2}$ mm.

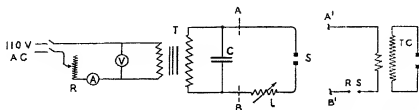


FIG. 3.27.—Electrical circuit for a spark source. Tesla spark indicated in A'—B' circuit.

Spark Sources. The nature of the electric spark is largely determined by the resonance system which can be set up between the condenser and inductance circuits, the usual source being that indicated in the diagram (Fig. 3.27), in which the capacity of the condenser (C) and the inductance of the coil (L) can be adjusted to yield the proper wave form or resonance

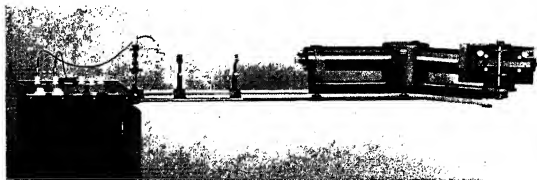


FIG. 3.28.—Spectrographic arrangement for spark analysis, showing spark generator, spark holder stand, condensing lenses, and medium spectrograph (Zeiss).

to the spark (Fig. 3.28). The variation of the spark conditions will yield what is known as a condensed or uncondensed spark, the two types being quite different in the intensities of spectral lines produced. The electrodes for spark analysis should, if possible, be pointed so as to keep the spark from wandering out of the optical path, and the gap should be from 3 to 6 mm in length, depending on the circuit conditions and the size of image desired on the spectrum slit.

The condensed spark will be more intense than the uncondensed spark, but will also have a great many more air lines, due to nitrogen and oxygen. The self-inductance in the secondary circuit will materially reduce the intensity of these air lines. The self-inductance is an open coil with adjustable taps to provide for various induction values. The action

of the self-inductance, like that of the arc circuit, is to prevent sparking at the first surge of current and maintain the spark as the current drops so as to provide a steadier and more uniform spark (Fig. 3.29). The self-

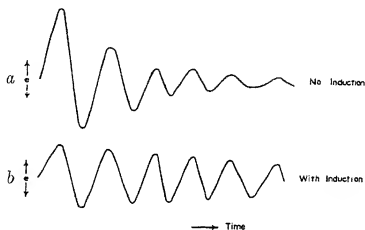


FIG. 3.29.—Oscillatory nature of a spark discharge (a) without induction and (b) with induction.

inductance will reduce to a slight extent the intensity of light emitted but will set up a more uniform oscillating system. The frequency of this oscillating spark may be expressed as

$$n = \frac{1}{2\pi\sqrt{LC}}$$

where n = oscillations per second; L , the self-inductance in henrys; and C , the capacity in microfarads. For a spark using a secondary voltage of 10,000 to 15,000 volts, a capacitance of 0.005 microfarad and inductance with a range of 0.02 to 1.5 millihenrys will be quite satisfactory. The self-inductance may easily be constructed as an open coil wound on a glass or insulating cylinder about 4 to 5 cm in diameter and with 50 to 100 turns spaced about 2 mm apart.

Comparison of Arc and Spark Sources. It is difficult to say which method of excitation is to be preferred, the arc or the spark, the choice being largely dependent on the available power supply, the character and the amount of the sample, and the type of lines which are desired. For low-melting substances, such as lead and tin alloys, Wood's metal, and similar products, the spark is to be preferred on account of the temperature conditions of the arc. The spark really involves a much higher atomic temperature than the arc, but a lower electrode temperature. For such low-melting substances an arc method can be used, but it may require intermittent exposures with cooling of the electrode, or the use of a carbon arc to hold the low-melting material while arcking. The spark is relatively free from the continuous background found in the

carbon arc (CN bands) between 3200 and 4200 Å (Fig. 3.30). The spark is better suited to the analysis of a minute amount of material or to the



FIG. 3.30.—Comparison of arc (A) and spark (S) spectra of iron N.

analysis of a spot on a larger metallic surface without disturbing the remaining surface. On the other hand, the arc is usually better suited

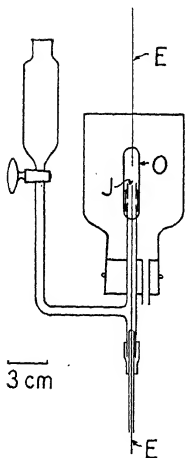


FIG. 3.31.—Spark arrangement for solutions showing electrodes, *E*; illumination opening in glass shield, *O*; and quartz jet, *J* (adapted from Twyman and Hitchen).

where a large amount of material is available but the concentration of the element sought is low. In other words, it is more difficult to burn up or sample an electrode by the spark method. Solutions lend themselves more readily to direct spark analysis since the electrode temperature is relatively low. The solution may be introduced directly into the spark through a separate tube (Fig. 3.31), it may be sprayed into the spark, or it may involve the use of the solution, if an electrolyte, as one of the electrodes. Then carbon, gold, or some inert metal with a relatively small number of lines may serve as the other electrode.

A laboratory equipped for spectrum analysis should have available both arc and spark methods so that one method can supplement the other.

Gaseous Discharge Source (Geissler Tube).

For the detection of the rare gases, He, A, Kr, Ne, Xe, as well as H, O, N, S, and certain molecular combinations, it is desirable to have available a discharge tube which can be filled with a gas at a low pressure. At low pressures, gases may be excited either by electrode or electrodeless discharge of a high-voltage current (a 30-milliampere 5000-volt neon sign transformer is ideal for this purpose) to

produce a characteristic high-voltage spark spectrum. In view of the fact that the intensity characteristics of the spectrum are markedly influenced by the excitation potentials of the elements present, it is difficult to apply quantitative or even qualitative analysis methods to gases. For example,

mercury, with a low excitation potential, will transmit practically all the energy in a tube containing neon and mercury, so that it is

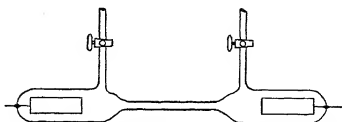


FIG. 3.32.—Discharge tube for spectra of gases.

difficult to show the presence of neon which has a very high excitation potential.

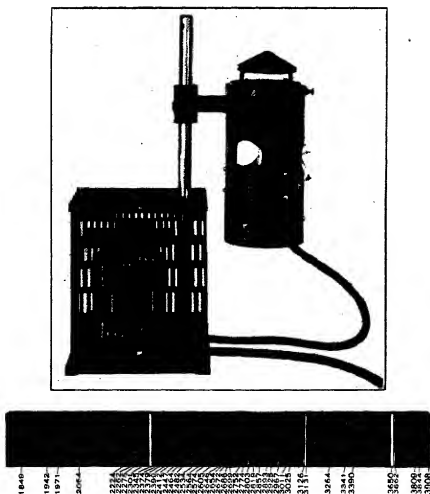


FIG. 3.33.—Hanovia Mercury Labare and ultraviolet spectrum produced. P.

For purposes of spectroscopic calibration and for standard reference lines, mercury, sodium, and neon tubes form a convenient light source. These lamps are available in glass or quartz, depending on the spectral

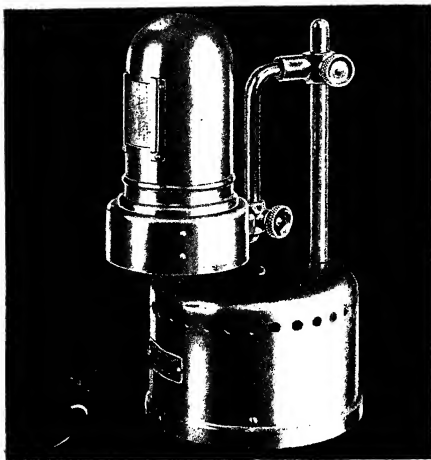
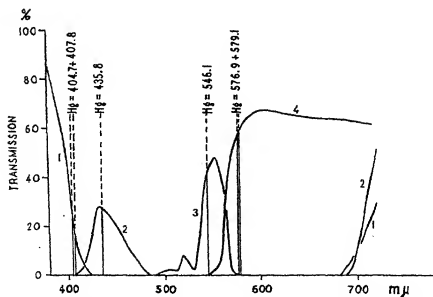


FIG. 3.34.—Sodium vapor lamp (General Electric Vapor Lamp Company)



3.35.—Transmission curves of monochromatic mercury lamp filters.

- (1) Corning "G 586 A," 3.20 mm.
- (2) " "Noviol A," 2.00 mm. + "G 585," 4.62 mm.
- (3) " "G 555 P," 8.5 mm + "G 34," 2.25 mm.
- (4) " "G 36 "

range desired and element contained. In recent years a number of these discharge lamps of a low-voltage, self-starting type have been developed (Fig. 3.36) which are very convenient as permanent laboratory standard lamps for the recording on the spectrogram of calibration lines much as the iron arc is used. In the red portion of the visible spectrum the number of iron lines is limited and the accepted secondary standards in this region

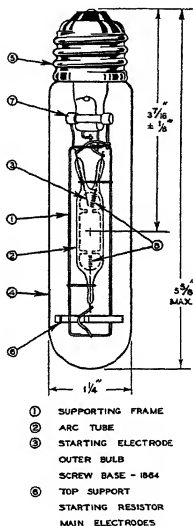


FIG. 3.36.—Mercury vapor lamp (Westinghouse).

include a number of neon lines. It is possible to fit adjacent to the slit of the spectrograph a small right-angle prism, covering only a portion of the slit, or fitted to swing into position when desired, so as to record from a permanent discharge tube attachment the comparison spectra without disturbing the equipment in the direct optical path of the spectrograph or spectroscope. With mercury discharge tubes (Figs. 3.33 and 3.36 one may interpose special filters to absorb the radiation from all the lines except one and thus produce a very good monochromatic light

source (Fig. 3.35). Having a set of these filters, one may dispense with a spectrometer in making a series of spectrophotometric measurements at the various mercury-line wavelength values.

LITERATURE

General

"Measurement of Radiant Energy." W. E. Forsythe and others (A15).

"Optische Methoden der Chemie." F. Weigert (A73).

Reference

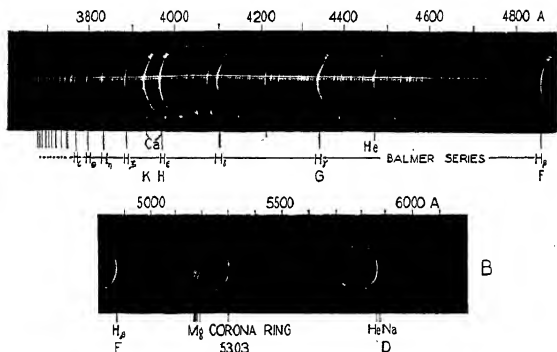
Baly (A3), Wood (A78), Twyman (A70), Scheibe (A59), Gerlach (A18) (A19).

Catalogs of Adam Hilger, Ltd.; Bausch and Lomb Optical Company; Carl Zeiss, Inc.; Gaertner Instrument Co.; and other makers of spectrographic equipment (see page 309).

CHAPTER IV

QUALITATIVE ANALYSIS, SPECTRUM TABLES, AND STANDARD SAMPLES

The application of spectroscopic methods to qualitative analysis dates from the work of Bunsen and Kirchhoff and other early investigators in the field of spectroscopy. The discovery that an element produced a characteristic spectrum quite naturally led to the idea that the same spectrum produced from an unknown was the result of the presence of that element in the unknown. Qualitative analysis was thus possible not only of substances immediately available to the chemist but also of any self-radiating body such as the sun or stars. The great developments in astrophysics have been largely the result of study of the spectra of



g. 4.1a.—Astronomical spectra, flash spectrum of the sun's chromosphere. P. (Taken by Menzel, Boyce, Brode, et al., Harvard Observatory-Massachusetts Institute of Technology Eclipse of the Sun Expedition to Siberia, Ak Bulak, Kazakhstan, U.S.S.R., 1936.) (Note the Balmer hydrogen series and the ring corona line.) A, third contact; B, second contact (inverted).

stellar bodies. The temperatures, mass, distance, speed of travel, direction of rotation of eclipsing pairs, and many other important facts, as well as the chemical composition of the radiating body, are determinable from spectroscopic data (Fig. 4.1).

As has been indicated in the discussion on the theory of line spectra (Chapter II), each element may be expected to give a large number of spectral lines, corresponding to the permitted electron jumps between various states and quantum values. In some elements such as hydrogen,



FIG. 4.1b.—Astronomical spectra, Fraunhofer lines in the sun spectrum (Mount Wilson Observatory, Carnegie Institution of Washington). N.

sodium, copper, and mercury, one may expect a rather simple pattern of singlet, doublet, and triplet systems; but in other elements, such as iron, tungsten, and molybdenum, one finds a very complicated set of

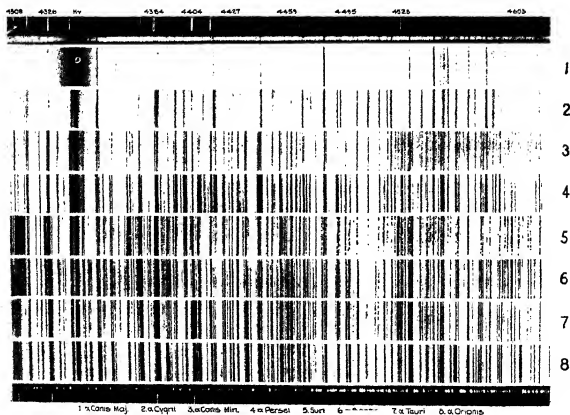


FIG. 4.1c.—Astronomical spectra, Widened prismatic coude spectra of stars of different spectral types. (Region 4300 to 4600 Å.) N. (Mount Wilson Observatory-Carnegie Institution of Washington.)

sextets, septets, and octets, and on account of this multiplicity there are a large number of lines. It is quite easy, then, to identify the spec-

trum of a pure sample of any substance, and it is also quite easy to identify the constituent elements of mixtures of substances of simple spectra (Fig. 4.2).

STANDARD LINES

The actual procedure in the identification of a pure substance may be that of comparison of spectra with a known pure sample of the same



FIG. 4.2.—Typical Spectrograms. P.

1. Tin. 2. Wood's metal. 3. Cadmium. 4. Zinc. 5. Molybdenum. 6. Nickel. 7. Copper.
8. Iron. 9. Aluminum bronze.

or suspected material, or one may measure the wavelength values of the observed lines and compare the measurements with the recorded data on known elements. The process of measuring the wavelength of a spectrum line may be accomplished by: (a) means of an interferometer and measurement directly of the wavelength of the line, (b) measurement of the relative position of the line between two known lines and interpolating the wavelength position, (c) the use of a wavelength scale which has been calibrated with the instrument and is photographically reproduced on the plate or visually observable in a direct observation, or (d) the superposition of a known spectrum with identified element lines either by projection of the spectrum or photographic recording in juxtaposition.

The measurement of lines by an interferometer method is very difficult and quite unnecessary for the identification of the wavelength of unknown lines in a qualitative analysis. The method is used, however, for the determination of the wavelength of a series of lines throughout the spectrum which are known as the primary and secondary standards. The primary standard has been chosen as the red line of cadmium which appears even in high resolution to be a single line. The wavelength of this line has been agreed upon as 6438.4696 Å in dry air at 15° C and 760 mm pressure, the radiation being produced in a vacuum tube with

electrodes. The selection and approval of such standards have been largely the work of astronomers and spectroscopists connected with the former International Union for Cooperation in Solar Research and the present International Astronomical Union, through a committee which is now headed by Dr. W. F. Meggers of the United States Bureau of Standards. The angstrom instead of being defined as 10^{-10} meter is now more accurately defined as $1/6438.4696$ of the wavelength of the cadmium red line. The accuracy of this determination is about 1 part in 10,000,000. For all practical purposes and for ease in indication, the angstrom may still be considered as equivalent to 10^{-10} meter.

A group of lines, for which three independent observers have obtained concordant results through interferometric measurement, have been accepted as the secondary standards (Table IV, lines indicated by "+"), and from these another set of lines has been measured by a process of interpolation, this latter set being known as tertiary standards (Table IV, lines indicated by "'"). Nearly all the secondary and tertiary lines are iron lines. Iron has been used extensively as a spectrographic standard because of the ease in obtaining pure samples, and also because it has a very large number of lines within the photographic ranges and the solar spectrum region (5500–3700 Å). With an extension of the photographic methods in both the infrared and ultraviolet regions, it has been found necessary to include other element lines such as neon and copper, to cover those parts of the spectrum where iron fails to give a sufficient number of lines.

These secondary standards do not supply a sufficient number of lines for convenient and accurate determination of the wavelength of unknown lines, and hence additional standards are often determined and accepted. (See the *Proceedings* of the International Astronomical Union for the Stockholm meeting, August, 1938, for additional accepted secondary and tertiary standards.) Tertiary standards are determined by accurate interpolation measurements between the known or secondary standard lines.

Following the work of Bunsen and Kirchhoff, Ångström measured accurately with three different gratings the wavelength values of the lines in the sun spectrum (Fraunhofer lines), and his assistant Thalen measured the principal lines of the then known metallic elements (44). Owing to an erroneous measurement of the length of the meter at Upsala as compared with the Paris meter, his values were found to be in error and he and his assistant corrected the original calculations so that the final work marked the first accurate reference map and element tabulation for spectrographic analysis. Cornu, in 1874–1880, published an extension of the Ångström solar map by a photographic method to include the near ultraviolet region. Other important contributions to the field of

spectroscopy and the extension of the spectral data beyond the visible regions were made by William Herschel, John Herschel, and Langley.

A definite improvement in accuracy was made in the solar spectrum map which was produced by Rowland through the use of gratings which he prepared. As the standard wavelength for his determinations, Rowland accepted the value 5896.156 Å for the sodium D line, a value which was the mean of a number of workers' observations, and which he felt, if ever shown to be in error, would require only a uniform correction of his data. Unfortunately, Rowland's data, although the most accurately determined material of its kind, had a periodic error which is greater than the experimental error with our improved present-day technique. Rowland's data have been corrected by members of the Mount Wilson Observatory Staff and published by the Carnegie Institution of Washington (458).

In 1894, Michelson, by means of an interferometer, determined accurately the wavelength values of three of the cadmium lines in the red, green, and blue portions of the spectrum and showed that these values did not agree with the Rowland map values within the limits of experimental error. The accuracy of interferometric measurements leaves no doubt but that measurements by this method are more acceptable than those made from calculation of grating space and relative dispersion. In view of the accuracy of the Michelson and the Fabry and Perot interferometric determinations on the red cadmium line, it has been agreed that this line shall be used as the primary spectroscopic standard. The accuracy of determination of this value is about 1 part in 10,000,000, which is comparable with that of the measurement of the standard meter. The accepted value of 6438.4696 Å for the cadmium red line also becomes the definition of the angstrom, in terms of the wavelength of this line.

TABLES OF SPECTRUM LINES ARRANGED BY ELEMENTS OR WAVELENGTH

The available lists of spectrum lines may be separated into two groups: those of a more condensed nature (*I*), and those which have attempted to cover all data of a known accuracy (*II*).

*I. Condensed Spectrum Line Tables**

1. "Wavelength Tables for Spectrum Analysis" by F. Twyman and D. M. Smith. These tables include (a) the distinctive lines in the spark spectra by

* See the Bibliography (pp. 315-325) for complete publication data on these and other references. The Bibliography is divided into three parts; *A, Theory of spectra and emission analysis; B, Absorption spectra; and C, Research publications and journal articles.* In each of these divisions the references are arranged in alphabetical order.

Hartley, Pollok, and Leonard; (b) the *raies ultimes* by de Gramont; (c) the sensitive lines by Ryde and Jenkins; and (d) the flame spectra lines by Lundegardh (1931) (A71).

2. "Atlas der letzten Linien der wichtigsten Elemente" by F. Löwe. A table of the persistent spark spectrum lines of the more important elements (1928) (A50).

3. "Tabelle der Hauptlinien der Linienspektren aller Elemente" by H. Kayser. A table of 19,000 lines representing 91 elements, arranged according to wavelength, a standard work for qualitative identification of arc and spark lines with intensities given on a 0 to 10 scale. The best available condensed spectrum line table (1926) (A41).

4. "Visual Lines for Spectrum Analysis" by D. M. Smith (1928) (A64).

5. "Table of Arc Spectrum Lines Arranged in Order of Wavelength" (1933) (A10), and "Metallurgical Spectrum Analysis" by W. J. Crook (1935) (A9).

6. "Die Spektren der Elemente bei normalem Druck," Vol. 1, by F. Exner and E. Haschek (1911).

7. "Emission Spectra of Elementary Substances" by H. Kayser. (In Vol. 5, pp. 276-322, of the "International Critical Tables" [1929] and also in the "Handbook of Chemistry and Physics" [1938].) A selected list of lines of 83 elements, arranged according to elements, giving arc and spark lines on an intensity scale of 1 to 10 (A22, A36).

8. "Wavelength of the Principal Lines in the Emission Spectra of the Elements" by J. A. Hannum. (In "Handbook of Chemistry" edited by N. A. Lange, pp. 863-887 [1937] [A23].)

9. "Chemische Spektralanalyse" by G. Scheibe. (In "Physikalische Methoden der analytischen Chemie" edited by W. Böttger, pp. 66-92 [1933].) A table of the principal lines of 62 elements, arranged according to wavelength, giving arc, spark, and flame lines on an intensity scale of 1 to 10 (A59).

10. "Tabellen zur qualitativen Analyse" by W. Gerlach and E. Riedl. (Vol. III of "Die chemische Emissionsspektralanalyse" by Gerlach [1936].) A table of the principal lines of 57 elements, arranged according to elements, with recommended control lines and possible interfering lines (A19).

11. The spectrum tables in this book, pp. 332 to 434, which have been selected from the above and other sources. These tables include the principal lines of 66 elements, arranged according to elements, giving arc and spark lines on an intensity scale of 1 to 10, and a table of the principal lines of 67 elements arranged according to wavelength, giving arc lines on an intensity scale of 2 to 4, 5 to 7, and 8 to 10.

12. "Wavelength Tables of 100,000 Spectrum Lines" by G. R. Harrison. A table of 100,000 lines from 2000 to 10,000 Å arranged according to wavelength. From the Spectroscopy Laboratory of the Massachusetts Institute of Technology with the assistance of the Works Progress Administration. To be published in 1939 (A27).

13. "Residual Arc Spectra" by W. F. Meggers and B. F. Scribner (C82). Tables of 50 to 60 elements giving the sensitive lines in an arc source (unpublished data compiled at the Bureau of Standards).

PHOTOGRAPHIC TABLES

II. Extended Spectrum Line Tables and Critical Compilations of Emission Spectrum Data

14. "Handbuch der Spektroskopie" by Kayser. Volumes 5 (1910), 6 (1912), 7 (1934), and 8 (1932) contain the most complete collected data on wavelength and intensity values of spectrum lines. The work is still quite incomplete as no data for 40 elements (from Nd to Zr) have been published since 1911 (A40).

15. "Die Spektren der Elemente bei normalem Druck" by Exner and Haschek (1911), Vols. II and III. The spectra of 77 elements, arranged according to elements, giving over 120,000 lines in arc and spark spectra on an intensity scale of 1 to 1000. (Wavelength values based on the Rowland scale.)

16. "Tables annuelles de constantes et données numériques," Section of emission spectra in Vols. I to XII (covering the literature from 1910 to 1936) giving about 800 pages of collected data (A68).

17. "Physikalische-Chemische Tabellen," Landolt-Bornstein, edited by W. A. Roth and K. Scheel, 5th edition (1923) and three supplementary editions covering the literature to 1934. These tables include an extended section on emission spectra and line spectra term analysis (A46).

Inasmuch as the data recorded in all these tables tend to become identical in character, the choice of the table to use will depend largely on the accuracy with which the analysis is to be made. The best published collections available at this time (1938) are the Kayser-Konen "Handbuch der Spektroskopie" (14) for the wavelength spectra according to elements, and the Kayser "Hauptlinien" tables (3) for the elements arranged according to wavelength. For most analytical purposes, however, the tables available in the chemical handbooks (7 and 8), the Twyman and Smith tables (1), the Scheibe tables (9), or the tables in this book (11) should be adequate. The publication of Harrison's 100,000 principal lines table (12) should provide an improvement over any of the available spectrum tables.

PHOTOGRAPHIC TABLES AND CHARTS

In addition to the numerical tables which have been described, a number of photographic tables are available. These may be divided into two types in accordance with their character or method of presentation.

III. Spectrograms of Elements

(Separate photographs of the spectrum of each element)

This form of presentation would correspond to the arrangement of line spectrum tabular data in accordance with the elements.

18. Eder, J. M., and Valenta, E., "Atlas typischer Spektren" (1911). Tables of flame, arc, and spark spectra **N** taken with glass prism, quartz prism, and grating. Includes 53 cards (12 by 16 inches) with 12 spectrograms on each card (A11).

19. Gatterer, A., and Junkes, J., "Atlas der Restlinien" (1937). Tables of the principal lines of 50 elements and 28 photographic charts (12 by 16 inches) with 6 spectrograms per chart. Photographs taken with prism dispersion including arc and spark spectrograms from 2200 to 8000 Å N (A17).

19a. Gatterer, A., and Junkes, J., "Arc spectrum of Iron from 8388 to 2242 Å" with "Spark spectrum of Iron from 4650 to 2242 Å" (1935). A set of 21 photographic charts (7 by 9.5 inches) taken with prism dispersion N (A17a).

20. Hilger, Spectrogram of Iron. A set of mounted photographic copies of a prism dispersion iron spectrogram P with the wavelength positions of the lines indicated. Eight cards (8 by 14 inches) (new edition 1937) (Fig. 4.3a) (A30).

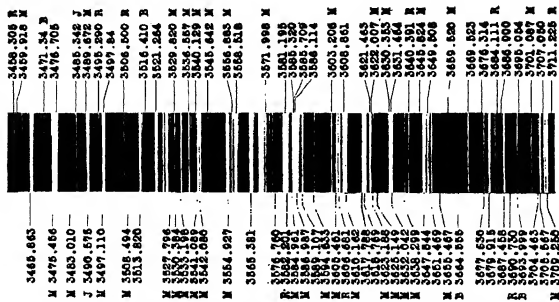


Fig. 4.3a.—Iron spectrum chart (Hilger). P. Prism dispersion (A30). Portion of series of 8 charts. Illustration shows one third of a chart reduced to half scale.

21. Hilger, Spectrogram of Copper. An enlarged spectrogram of copper from 2043 to 5782 Å. Three cards (6 by 14 inches) P (A31).

22. Hilger, Spectrogram of Neon. Enlarged spectrogram on a card (5 by 8 inches) showing 20 lines from 5850 to 7032 Å P (A32).

23. Hilger, Spectrogram of Helium. Enlarged spectrogram on a card (4 by 12 inches) showing 19 lines between 3610 and 7282 Å P (A33).

24. A privately printed iron arc spectrum chart by Professor G. R. Harrison comprising 18 cards (each 20 inches in length) prepared by direct printing from spectrograms made on a 10-meter focal length, 30,000-line grating, is especially valuable for workers using higher orders of grating instruments since it charts three overlapping orders N (A28).

IV. Composite Spectrogram of Elements

This form of presentation is subdivided into two types: *a*, spectrograms obtained from a mixed source; and *b*, indicated positions on an iron spectrum or scale as to where element lines would appear if present.

must be admitted that the identification is easier when the chart and spectrogram are produced by the same dispersion method.

The available charts which correspond to the numerical tabulation of lines of all elements arranged according to wavelength, rather than those arranged according to elements, are of two types: those showing the principal lines of a large number of elements, and those showing only the iron spectrum and the indicated position where the principal lines of elements would be if they were present in the spectrum. The use of iron in this way essentially constitutes a very finely divided though somewhat irregular scale which can be impressed or printed in juxtaposition to, or partially overlapping, the unknown spectrum, and thus serves to locate the position of unknown lines.

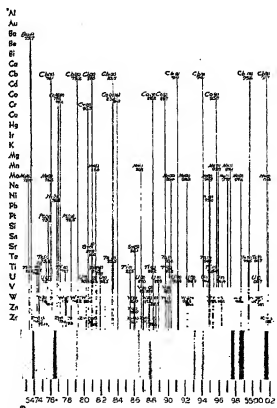


FIG. 4.4.—Iron—unknown spectrum chart (Crook). N. Grating dispersion ($A 10$). Portion of series of 20 charts. Illustration shows one half of a chart reduced to one third scale.

The selection of the lines to appear in charts of the first type which give only a few lines of all the elements is dependent on a principle proposed by de Gramont, known as the *raies ultimes*, which will be discussed later in this chapter, but for the moment we may accept these as the most persistent lines of the various elements which are included. An excellent chart of this type, known as the *raies ultimes* chart (25), is available

SPECTROGRAM CHARTS

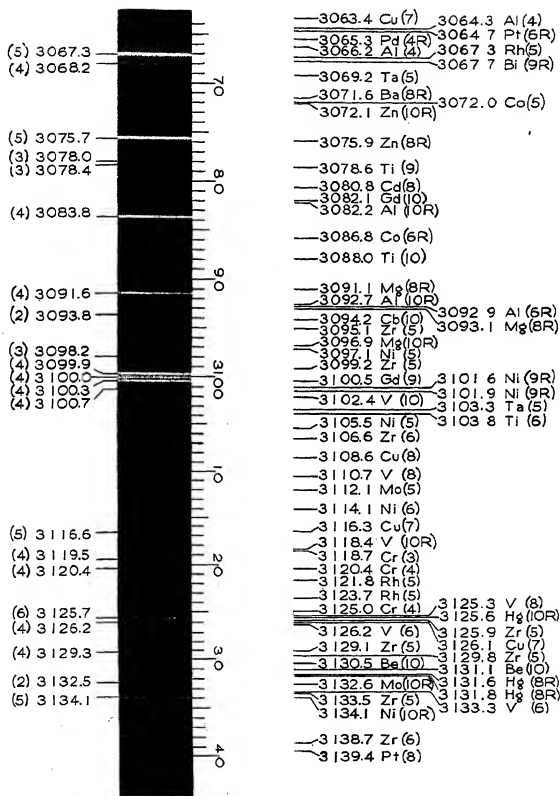


FIG. 4.5.—Chart for spectral analysis with iron comparison (Brode). P. (See Plates II to XXXVI in this book for complete series.)

from Adam Hilger, and in addition, this company has prepared a powder of a large number of elements so as to enable workers to prepare their own negatives for direct photographic or projection comparison (Fig. 4.3*b*).

The second type of chart, that of an iron spectrum with indicated positions of lines of other elements, is of importance in the rapid identification of lines in qualitative analysis of unknowns. Three charts of this type are available; two of which, the Bardet (28) and those in this book (30), are for prismatic instruments, while the Crook (29) (Fig. 4.4) is for a grating dispersion. The Bardet table is limited to a range from 2500 to 3570 Å, and the Crook table from 2790 to 3430 Å and from 5050 to 5670 Å. Those in this book have been designed to cover a wider range, from 2310 to 5080 Å.

PERSISTENT LINES (RAIES

All these iron-unknown tables give line intensities as well as position of the unknown lines. The selection of lines for inclusion in such tables is usually the somewhat random choice of the compiler of the table, although an attempt is made to include the strongest lines of all the possible elements. Outside the tables of persistent lines or the raies ultimes there has been no attempt to prepare condensed tables and charts based on a nonarbitrary selection, except in the tables of Meggers (13), in which the "residual lines" are selected in accordance with their presence in diluted samples in arc spectra.

De Gramont has suggested a special name for the most persistent lines of an element: the raies ultimes; they are also known as the letzten linien, or the persistent lines. As one dilutes the amount of an element in an arc, the number of lines observable is reduced and ultimately there remain only a very few lines of the element which is diluted. These lines are thus known as the raies ultimes or persistent lines. Data have been collected for a large number of elements in a special table of persistent lines (Tables I and II). The persistent lines are not necessarily the strongest lines in the spectrum, nor are they always the lines which require the least energy of excitation, i.e., the resonance lines. They are determined by a general rule proposed by Meggers and Scribner (13); that a persistent line originates in a simple interchange of a single electron between an *s* and a *p* state, usually preferring configurations in which only one electron occurs in these states. In many of the condensed tables which are available for spectroscopic examination the persistent lines are either listed separately or indicated with a prime (') or letter (*p*) or (*P*), the most persistent lines being indicated by (*P*) and the next most persistent by (*p*).

From this discussion on the persistent lines it is apparent that in the

qualitative analysis for a certain element one need only look for the persistent lines of that element. If they are absent the assumption may be made that the element is not present in the sample.

QUALITATIVE ANALYSIS

The spectrum photograph may be obtained by direct arcing or sparking of a conducting sample or by the use of a carbon or other conducting electrode as a holder, and introducing the material on the electrode. If the instrument has a printable scale it should be recorded on the negative, and on the other side of the spectrogram of the unknown one should



Fig. 4.6.—Spectrograms of common materials. P.

1. C + Sb. 2. C + Bi. 3. C + Sr. 4. C + Ca. 5. C + Mg. 6. C + Na + K. 7. C.
8. Wood's metal. 9. Solder. 10. Pt. 11. Coin silver. 12. Mn. 13. Co. 14. Pb.

photograph a spectrum of a known element or compound, such as iron, copper, a known brass, "R-U" powder, or a sample of the principal constituent of the unknown (Fig. 4.6) (See Exercise 2, Chapter XII).

In the analysis of a brass sample (Fig. 4.7) the reproduction of a copper spectrum adjacent to a brass photograph enables the observer to mark



Fig. 4.7.—Spectra of 1. aluminum (spark); 2. aluminum bronze (arc); 3. copper (arc); and 4. brass (arc). N.

at once all lines due to copper, assuming, of course, that the copper sample is spectroscopically pure. For routine analytical work the operator will have available negatives with the copper or other element lines identified so that the negatives may be compared simultaneously by projection or other methods. A convenient method of examination, especially if the dispersion of the instrument is low, is to make enlarge-

ments from 5 to 10 times the size of the original negative, mount the enlargement on a suitable card, and write in the lines as determined (see Fig. 12.5, page 241). For instruments which do not contain a graduated scale, and for more exact analysis, one may photograph an iron spectrum adjacent to the unknown. This in itself acts as a finely, though irregularly, graduated scale. Photographic charts indicating lines of elements in relation to iron (page 69 and Plates II to XXXVI), have been prepared for this purpose. Those which are included in this book (although one half the size commonly used in analytical work) have been designed to enable the operator to use a strip enlargement of the spectrum or to project his spectrum in the blank space between the iron spectrum and the unknown lines. By experience it has been found that this method is both rapid and accurate, and it is much more convenient to apply, especially to student instruction, than the microscopic examination of the original plate, if a large number of lines are to be identified (see section on photography, page 300).

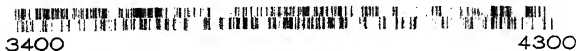


Fig. 4.8.—Portion of iron spectrogram (bottom) and nonferrous alloy (top). N.

The procedure of qualitative analysis may be roughly divided into two parts: (a) search for a definite element, and (b) identification of unknown elements. In the search for a definite element, the use of the persistent lines should be sufficient to confirm the presence of the element, although in samples with a large number of lines the overlapping which may occur, especially with a low-dispersion instrument, may make these uncertain. At least three lines concerning which there is no possible doubt as to origin, should be identified so as positively to identify the element.

The identification of unknown elements requires a more complete identification of all the spectral lines, except those which may be eliminated by means of a pure standard photograph and visual comparison. It can be seen that in working with a nonferrous alloy unknown (Fig. 4.8) a pure-iron comparison spectrum would relieve the analyst of a great amount of measurement and identification work. A considerable amount of labor can also be avoided by the identification of strong lines of impurities not present in the comparison spectrum, and then, from the tables giving the lines of that element (Table IV), the remaining weaker lines of the element may be rapidly identified and eliminated. It may also happen that there are available in the laboratory photographs of

pure samples of this impurity element so that direct comparison of photographs or prints may enable the analyst to eliminate a large group of lines. For the remaining lines, and often this procedure may apply to the entire negative, the wavelength should be determined from the scale or comparison (iron) spectrum and the possible elements for each line tabulated, consulting either photographic tables or, for more complete analysis, such tables as the Kayser "Hauptlinien" (A41), the Massachusetts Institute of Technology 100,000-line table (A27), the Scheibe table (A59), Twyman table (A71), or the table in this book (Table III). Some of the available tables indicate the position of occurrence of the next strong line of the same element so as to enable the operator to make a rapid confirmation of the assigned element.

LINE IDENTIFICATION

Experience will show that it is not possible by visual comparison of negatives from medium-dispersion instruments (2000 to 7000 in 25 cm)

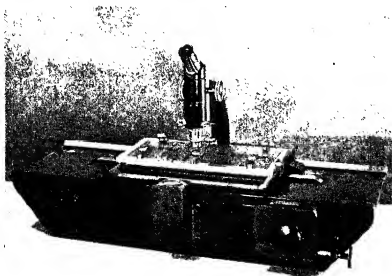


FIG. 4.9a.—Spectrum comparator (Bausch and Lomb).

to assign the position of the line closer than one or two angstrom units; hence, as can be seen in Table III, there may be a number of possibilities which can be eliminated in part by a search for the persistent lines of the elements which are possible. For very accurate analysis it may be necessary to determine the position of the unknown line more accurately. This may be accomplished by means of measuring devices such as a traveling microscope or micrometer eyepiece (Fig. 4.9). With grating instruments it is possible to make an interpolation measurement on the

negative, between two or three known lines, and thus determine the wavelength. With prism instruments, in which there is a rapid change of dispersion with wavelength, a more complex formula (Hartmann formula) is used in which three known lines are required.

$$\lambda = \lambda_0 + \frac{c}{(n - n_0)^{1/a}}$$

where λ is the wavelength of the line in question; n , the index of refraction of the dispersing medium at the wavelength in question; and λ_0 , c , n_0 , and a are constants. For purposes of calculation the value of a may be assumed to be unity, and in place of the refractive indices one may use the micrometer readings on the plate for the unknown line s and the known line s_0 . The equation then becomes

$$\lambda = \lambda_0 + \frac{c}{s + s_0}$$

which can be solved by measuring the micrometer values for the separation between the unknown line and three adjacent known lines (chosen so that not all are on the same side of the unknown line).

For all but the most exacting measurements it is possible to plot the known wavelength values against the micrometer readings and inter-

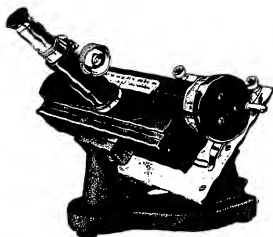


Fig. 4.9b.—Spectrum comparator (Gaertner).

polate for the wavelength value of the unknown as determined by its micrometer reading. Over very limited spectral ranges, especially with instruments of high dispersion, linear interpolation may be used with sufficient accuracy for the usual identification. For all grating work, even where the system may be in the Eagle mounting or any other form which does not produce an exactly linear dispersion, the use of direct linear interpolation is satisfactory for element identification. One seldom

uses the Hartmann formula unless the assignment of wavelength to an unreported line or the most exacting identification requirements are involved.

STANDARD SAMPLES

For the purpose of superimposing, or printing in juxtaposition, a spectrogram of a known standard substance, it is desirable to have available special standard samples, similar to the analytical standards supplied by the Bureau of Standards for gravimetric analysis. Standard samples are available from a number of sources: the large-scale commercial producers of high-grade products as well as laboratory supply houses. Special mention should be made of the Hilger samples of metals

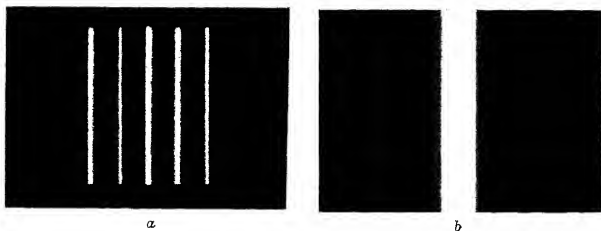


FIG. 4.10.—Examples of spectrum line combinations for rapid identification.

- a. Magnesium group of five symmetrically spaced lines at 2780 Å. P.
b. Beryllium doublet at 3130.48 and 3131.13 faint lines are ghosts from grating.
(Crook.) P.

and salts which have been prepared for spectroscopic standards. A subcommittee of the American Society for Testing Materials committee on spectrographic analysis under the direction of T. A. Wright has prepared a list of such samples for metallurgical identification (C131).

In the rapid qualitative analysis of a large number of samples one soon learns to recognize certain groups of lines so that one can identify their position on the negative in the absence of a scale, or confirm at once the presence of an element. The extensive use of the iron spectrum as a calibrating scale makes it useful to be able to identify the section of the spectrum, especially if the negative is taken on a Littrow instrument in which only a portion of the spectrum appears on any one negative. For example, in the section at 3100, a strong triplet followed by four evenly spaced intense lines should be easily identified (Fig. 4.5). Another easily identified group is the double-single-double-single group

at 2404-2413. The copper doublet at 3247-3274, and the magnesium group of five lines at 2776-2783 (Fig. 4.10), are also very distinctive. A

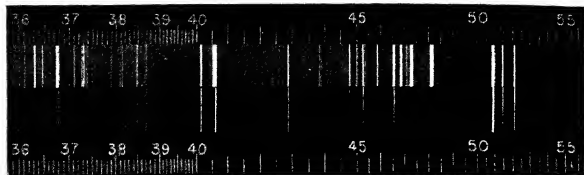


FIG. 4.10c.—Zinc group of three lines at 4680, 4722, and 4810 and lead line at 4058 in a brass sample (upper spectrogram). Note characteristic copper group of three lines at 5105, 5153, and 5218 and the pair of lines at 4022 and 4062. P.

manganese group of three lines at 2794-2801, aluminum pairs at 3082-3092 and 3944-3961, and many other lines are easily recognized, and

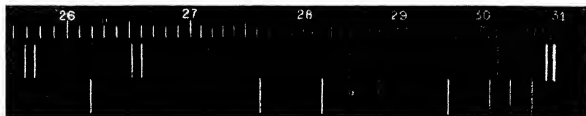


FIG. 4.10d.—Aluminum doublets (upper spectrogram) and copper comparison (lower spectrogram). P.

the experienced analyst should have little difficulty in identifying many elements by a superficial examination of the spectrogram.

LITERATURE

General

"Metallurgical Analysis by the Spectrograph." D. M. Smith (*A63*).

"Spectroscopy in Science and Industry." S. Judd Lewis (*A47*).

"Chemische Spektralanalyse." G. Scheibe (*A59*).

Reference

Gerlach (*A19*), Kayser (*A40*), Seith and Ruthardt (*A62*), Lowe (*B37*).

Spectrum tables listed on pages 63 to 67.

CHAPTER V

QUANTITATIVE EMISSION ANALYSIS

DEVELOPMENT OF QUANTITATIVE METHODS

The early use of spectroscopic methods in the qualitative identification of elements naturally led to the consideration of quantitative determination by this same method. Lockyer was one of the first workers to propose the use of the spectroscope for quantitative analysis. His suggestion involved the determination of the length of the spark lines at each electrode as a measure of the concentration of the element. The classical publication of Hartley some ten years later in 1884 (*C63*) on the persistent lines of Mg, Zn, Cd, Al, In, Tl, Cu, Ag, Sn, Hg, Pb, Te, As, Sb, and Bi paved the way towards the field of quantitative analysis by indicating a correlation between element concentration and line intensity. Over twenty years later Pollok and Leonard continued Hartley's investigations by the publication of a series of seven papers on the spark spectra of a number of elements at low known concentrations, and a determination of the principal lines of elements in the spark spectra. Hartley, Pollok, and Leonard (*C76, C95*) used a solution system in which they indicated lines which were present in one concentration but not in concentrations of one tenth that amount, employing a definite sparking time and current density. The series used was as follows:

TABLE 5.1

LINE DESIGNATIONS USED BY HARTLEY (*C63*)

τ	= lines present in the pure sample but not in a strong solution
σ	= lines present in a strong solution but not in a 1.0% solution
ϕ	= lines present in a 1.0% solution but not in a 0.1% solution
χ	= lines present in a 0.1% solution but not in a 0.01% solution
ψ	= lines present in a 0.01% solution but not in a 0.001% solution
ω	= lines present in a 0.001% solution but not in a 0.0001% solution

De Gramont (*C40, C41*) published a number of papers during the first quarter of the present century, most of which deal with the persistent or *raies ultimes* lines and their application to spectrum analysis. In 1920 he published his table of persistent lines (*raies ultimes* or *letzten linien*) (see Table I in Appendix), which was an important contribution to both

qualitative and quantitative analysis. In this table of persistent lines, de Gramont indicated the *raies sensibles* and *raies ultimes* as the persistent lines in the visible and ultraviolet regions respectively. The term *raies ultimes* has since been applied to persistent lines in both these spectral regions.

WORK OF MEGGERS, GERLACH, AND SCHEIBE

Meggers, Kiess, and Stimson published in 1922 (*C81*) a series of quantitative spectrographic determinations on samples of tin, gold, and platinum, using the methods which de Gramont originated in 1895. For a quarter of a century, de Gramont had been almost the sole proponent of this analytical procedure. In this paper by Meggers and his co-workers, alloys of known concentration were used as standards, such as a platinum series containing the following rhodium concentrations: 1.0, 0.5, 0.01, and 0.001 per cent. The unknown sample of platinum was sparked in a condensed spark in accordance with the de Gramont method, and the spectrogram obtained was compared with spectrograms obtained under similar sparking conditions from the known standards. The density of the persistent lines or *raies ultimes* served as a measure of the amount of rhodium in the unknown sample. Similar standards and density determinations were made on a series of gold samples containing from 1 to 0.001 per cent of silver, copper, iron, and lead. In the analysis of fusible plugs of tin it was shown that one might expect such impurities as lead, zinc, antimony, copper, iron, arsenic, and bismuth. A comparison of the results obtained by spectrographic and chemical means (Table 5.2) demonstrated that this new method was capable of giving quantitative results

TABLE 5.2

COMPARISON OF SPECTROGRAPHIC AND CHEMICAL ANALYSIS OF TIN ALLOYS (*C81*)

Sample	%—Spectrographic							%—Chemical			
	Cu	Pb	Fe	Zn	Ni	Ag	Bi	Cu	Pb	Fe	Zn
3993	0.1	0.1	0.005	0.001	0.001	0.000	0.000	0.08	0.10	0.03	
4409	0.6	0.05	0.1	0.07	0.001	0.000	0.000	0.62	0.04	0.04	0.06
4148	0.4	0.08	0.07	0.005	0.001	0.000	0.001	0.45	0.10	0.09	
4199	0.8	0.6	0.02	0.04	0.01	0.001	0.01	0.76	0.53	0.02	
4247	0.6	1.0	0.01	0.15	0.01	0.001	0.01	0.65	0.98	0.042	

with considerable precision. "In fact, the precision probably surpasses that of the chemical gravimetric method in a case of this kind, for it is

precisely for the small quantities for which weighing errors are large that the spectral methods show their greatest sensitiveness. The greatest economy, however, is in materials and time. Whereas a chemical analysis will require about 10 g. of material, only a few milligrams are consumed to make a spark spectrum. A dozen samples carried along simultaneously require about two days for a chemical analysis. The same can be accomplished in two hours by the spectral method" (Meggers, Kiess, and Stimson) (C81).

The actual determination of line intensity was made by a visual comparison of the unknown-sample persistent line with the series of photographs of the known-sample persistent line. This measurement of comparative density of two lines can, of course, be made visually or by some mechanical or electrical means. Much of the improvement that has been made in the spectrographic quantitative methods, since the pioneering work of Meggers, has been in the direction of increased accuracy in measurement of line intensity or density.

PHOTOGRAPHIC MEASUREMENT OF LIGHT INTENSITY (415)

Line intensity may be measured in a number of ways, nearly all of which are photographic in character. The photographic emulsion produces a blackening on the developed negative which is not directly proportional to the light intensity affecting the silver halide, but, as can be seen from the $d/\log I$ curve (Fig. 5.1), is, for a considerable intensity range, a linear function of the log of intensity. This linear range provides a means of interpolation between known light concentration or intensity values, provided, of course, that the conditions of exposure are so regulated that the density of the line in question falls within the limits of this linear slope.

Two sources of error should be considered when using the photographic method of intensity comparison. In the first place there is what is known as the reciprocity failure, which may be expressed as the failure of photographic emulsions to conform to the relation

$$\log I \cdot t = d \quad (\text{where } \log I \cdot t = \text{a constant})$$

where I = intensity, t = time of exposure, and d = density of the image

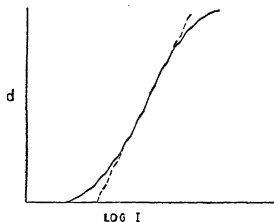


FIG. 5.1.—Variation of density (d) with light intensity (I) of a photographic emulsion.

formed. It can be shown that there is an optimum exposure time, requiring a minimum light intensity for unit density, and an optimum light intensity, requiring a minimum exposure time, for a given emulsion. For intensity or time values differing from this optimum value, a greater value of $I \cdot t$ will be required to produce the same unit density.

The second possible source of error, which results from the reciprocity failure and the inertia of the photographic process, is known as the intermittency effect. If an exposure of 100 seconds with a given source is required to produce a unit density of photographic image, then ten separate exposures of 10 seconds each should produce the same density. The failure to obtain the same density is known as the intermittency effect. It has been shown, however, that if the number of interruptions (sector revolutions) is greater than about 20 per second or the total number of interruptions in an exposure is greater than 50 there is no great intermittency effect and the errors from both these sources will, in their application to quantitative spectrographic analysis, be less than the usual errors in observation.

INTERNAL STANDARDS

The uncertainty with regard to the relation between density and logarithm of intensity may be eliminated if the element line in the unknown can be compared with the same line in a series of samples with known varying concentration and in which one of these series gives the same line density as the unknown sample. It is obviously impossible to incorporate within the unknown sample a definite amount of the known material for which the test is being made. To accomplish this comparison, it becomes necessary to refer the intensities of the lines in the known and unknown samples to some common line of an extraneous element which remains unchanged in both spectra. This method of "internal standard" control was first developed by Gerlach (*A19a*). Two types of internal standard lines may be used: (a) a weak line of the element which is the major constituent of the sample, which line is known to be constant in intensity, within the limits of experimental observation, and (b) a strong or persistent line in the spectra of an added small amount of an element which is known not to be present in either the known or unknown sample. The observed lines can then be classified in pairs of equal intensity, i.e., known or internal standard line, and unknown line. The preparation of a series of standard samples with a varying concentration range of the "unknown" element and observation of the spectra of these samples provide data for the selection of a series of these pairs to cover any desired concentration range. Since both the unknown and the internal standard are a part of the same sample, it is obvious that variation in

the time of exposure, plate characteristics, or developing conditions will not affect the relative density of two lines which are equal in intensity in the light source.

One condition which will influence the relative intensity of a pair of such lines will be a variation in the excitation conditions of the arc or spark, if the two lines are chosen so as to represent markedly different energy conditions in the arc or spark. For example, one line may be due to a singly ionized atom of low potential of excitation and the other to a doubly ionized atom which requires a high ionization potential (Fig. 5.2). An increase in the temperature or voltage would favor the latter

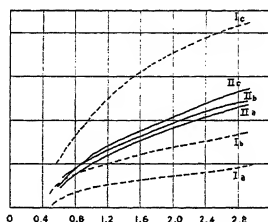


FIG. 5.2.—Comparison of working curves from lines representing similar excitation response (I) and different response (II) (Scheibe [C104]).

line and reduce the intensity of the former. For further control and as a means of increasing the accuracy of the observations, definite arc or spark conditions are maintained, and, in addition, one may define the conditions spectrographically, i.e., choose a pair of lines, representing low and high excitation conditions of the same atom, which are equal in intensity under the prevailing spark or arc conditions. This condition of spectral character may then be added to the internal standard pair equality as a guide to a fixed concentration ratio of known and unknown lines (Table 5.3).

HOMOLOGOUS PAIRS

A second method of avoiding the possibility of error due to a change of arc or spark conditions is to choose for the known internal standard line and the unknown comparison line, which are to be of equal intensity for a given concentration, lines which are known to have approximately the same excitation conditions so that within a considerable change in arc or spark condition any change which may take place in one line

intensity will also take place to the same extent in the other. Such a pair of lines has been defined as an "homologous pair" (*A18, A19*). The choice of homologous pairs of lines for spectral analysis may be made by a study of known standards under varied conditions of arc or spark (variation of voltage, inductance, capacity, etc.), and once these pairs have been established it becomes possible to eliminate some of the errors involved in earlier quantitative analyses. For more exact determination of homologous pairs one may, of course, revert to the spectral analysis of the individual elements, determining the term, levels, multiplicities, etc., and may choose from similar conditions the lines to be compared.

TABLE 5.3

HOMOLOGOUS PAIRS AND CONTROL STANDARDS FOR ANALYSIS
OF BISMUTH IN LEAD

(Gerlach and Schweitzer) (*A19a*)

Excitation control pair
Sn II 3352.3 = Sn I 3330.6

Ph	Bi	%Bi
2657.1 =	2730.5	5
2657.1 =	2780.5	1.5
3220.5 =	3024.6	1.5
3220.5 =	3067.7	0.07

Having once chosen a pair of lines which are known to be of equal intensity for a definite concentration ratio, regardless of the excitation

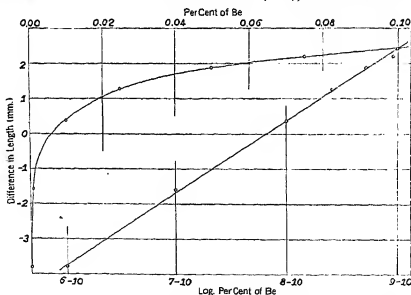


FIG. 5.3.—Working curve for determination of beryllium (3132.3 Å). Bismuth internal standard (3067.7 Å). (Brode and Stead [*C31*].)

conditions within the experimental limits of variation, or a pair of lines which are known to be of equal intensity for a definite concentration

ratio, at a definite excitation condition which can be controlled, one is confronted with the possibility of variation of the "unknown" concentration. Since the photographic negative, over an appreciable range, has a linear relation between the negative density and the logarithm of the light intensity, and since the amount of the element and the intensity are, by definition of method and control, concomitant, one may measure the relative density of the known and unknown lines and thus may construct a working curve for the element over a considerable concentration range of the unknown. Thus the determination is not limited to a series of definite concentrations by the equal intensity method. In the graphical representation of a working curve (Fig. 5.3) one may plot the logarithm of the concentration of the unknown against the ratio of the densities (which is a linear function of the logarithm of the concentration or light intensity), and in such a case one should obtain a straight line over the concentration range within which the method is applicable.

LOGARITHMIC SECTOR

Scheibe presented a fundamental contribution to the practice of quantitative spectroscopic analysis when he introduced the use of a logarithmic

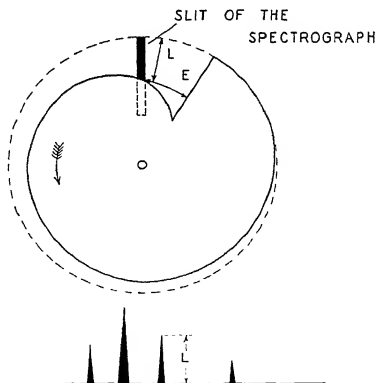


FIG. 5.4.—Logarithmic sector (appearance of spectrum lines of different intensity indicated below).

mic sector in front of the spectrograph slit (104, 105). The use of step or linear sectors or filters in front of a spectrograph slit as a means of

measuring intensities was not original at the time, but this was the first application to quantitative analysis. Hamburger and Holst (*C57*) had previously used a logarithmic sector in front of a spectrograph slit for the determination of intensity ratios in multiplets. The sector may be cut either in a smooth curve, which is equivalent to an infinite number of steps (Fig. 5.4), or in a finite number of steps (Fig. 5.5). The step sector limits the measurements to certain density levels but, in turn, permits the application of density photometers to the measurement of the blackening of the photographic plate. Neutral wedges may also serve the same purpose as rotating sectors, and these may be either of continuous or stepwise gradation. Partially silvered mirrors are not suitable on account of the ultraviolet transmission of silver films, but the evaporated

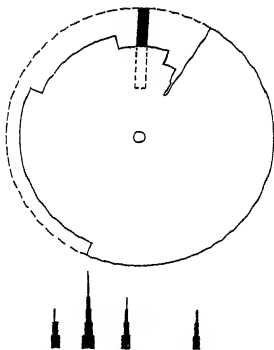


Fig. 5.5.—Step sector (appearance of spectrum lines of different intensity indicated below).

aluminum, antimony, or sputtered-platinum mirrors are quite satisfactory for this purpose. Since within certain limits the width of the spectrum line, produced from a uniform light source projected on the slit, remains constant, but the photographic density increases as one increases the slit width, one may use a step or sloping slit in place of a step sector in front of the slit. Such a slit is difficult to operate since it must be kept at a definite width in order that the step ratios will bear the proper relation to each other. Vierordt (*C118*) has designed a special two-step slit of this type, involving two separate jaws operating against a common jaw so that the slit widths could be set to any desired ratio.

Hansen, Scheffer, and Duffendack and Wolfe have proposed step slits with more than two steps but lacking the ability of adjustment of the ratio between step widths. Such a series of slit widths can best be produced by ruling a series of superimposed lines on a metallized quartz plate, each line in the series being shorter by a definite amount and broader by a definite amount compared with the preceding line so as to

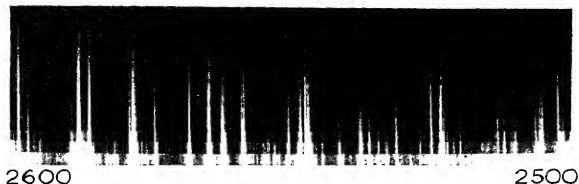


Fig. 5.6.—Step sector spectrogram (steel sample). P.

produce approximately a logarithmic difference in the light transmission. The actual width of the lines is not of extreme importance since the slit can be calibrated against standard density wedges (Fig. 3.15).

In the application to grating instruments where the character of the mounting prevents the use of a sector or wedge at the slit, one may place such a device at the focal point of the grating or immediately in front of the negative. With the second arrangement it is necessary to

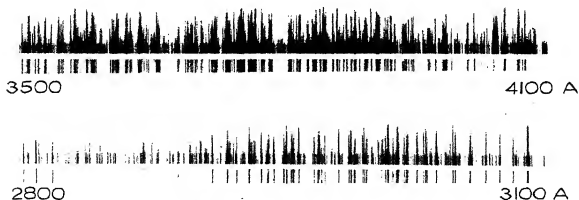


Fig. 5.7a.—Logarithmic sector spectrogram (steel sample). N.

have a cylindrical rotor so as to reduce equally the intensity of all lines on the plate. Such a rotor, usually a hemicylindrical segment of a solid cylinder, may also be placed in front of a quartz spectrograph slit, where it will produce a double set of tapered lines.

All these step or gradient sectors, slits, and density wedges produce

the same type of effect on the photographic plate, namely, a spectrum line of graded density, the degree or character of the density change being dependent on the type of the device. Step sectors, step slits, and step wedges produce lines with a definite series of density steps (Fig. 5.6), whereas smooth sectors, wedges, and slits, which are the equivalent of an infinite number of steps, produce a gradual density change in the line.

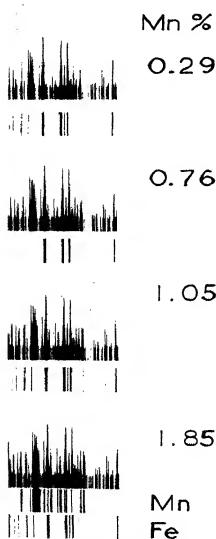


Fig. 5.7b.—Logarithmic sector spectrogram (steel sample).
N.

While all types of these reducing devices can be calibrated in terms of relative density per step or height of line from a given base, it has been found extremely convenient to cut or make the gradient device with a logarithmic extinction factor. For a step or smooth sector, this can be done by use of a logarithmic curve or steps in preparation of the sector.

An important prerequisite of the gradient line method (the use of a logarithmic sector, stepslit, density wedge or rotor in front of the negative) is that the slit should be uniformly illuminated along its entire effective length. The use of a lens system which projects an image of the arc or spark on the slit is obviously unsatisfactory since the line density varies within an arc or spark unless only a very small portion from the center of the arc or spark can be used and projected with a long-focus lens to furnish a rather large image on the slit. A method quite often employed with considerable success is to place a lens as near as possible to the slit and sector. This lens should be of such a focal length as to focus the light source on the collimating lens of the prism. In order to eliminate electrode ends or other parts of the arc or spark, a suitable diaphragm can

be inserted at this point (Fig. 5.8). Other suggested methods include substituting a cylindrical condensing lens for a spherical lens for illumination of the slit; the omission of the condensing lens; and focusing the light source on a diaphragm so as to select the center portion of the arc or spark, and then projection of this illuminated diaphragm on the slit in a sufficiently large image to approximate parallel light.

The logarithmic wedge or sector reduces the intensity of the light

passing through the slit, and, assuming that the photographic plate is capable of integrating intermittent exposures so as to compare exposures of shorter time and greater intensity with longer time and weaker in-

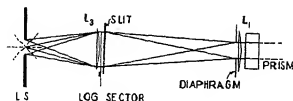


FIG. 5.8.—Optical arrangement for use of logarithmic sector or diaphragm at the slit.

tensity, an equal blackening of the photographic plate will be produced at points along the graded spectrum line where the light intensity is the same. The measurement of density is affected through a measurement



FIG. 5.9a.

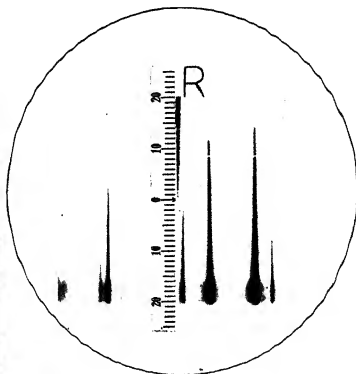


FIG. 5.9b.

FIG. 5.9a.—Spectrum measuring magnifier (Bausch and Lomb).

FIG. 5.9b.—Special eyepiece for line density matching. Inverted comparison line and scale are part of the field of the reading glass. (Wilhelm [C120].)

of the length of the graded line. The intensity of two lines at the pointed end will be the same, and, if the relative exposure has been produced by a logarithmic device, then the length of the line from a given reference

point will be a logarithmic function of the intensity of the line in the source (*C114*).

In the comparison of two lines such as an internal standard and an unknown line, the length of each line will be a measure of its intensity and the ratio of the logarithm of the intensities can be expressed as $\log I_s - \log I_u$. With a logarithmic sector each line becomes a logarithmic intensity measure and the difference in length of the lines expresses the intensity ratio. This difference, as can be observed by experiment, remains the same for various conditions of exposure, slit width, development, and plate characteristics, as long as the sector or wedge gradient is sufficient to include the transmission or opacity values required to produce the same selected density in both lines. It is not necessary to use the point of extinction for matching, and a method has been suggested (Fig. 5.9b) in which a reverse graded line or pair of lines has been used in the micrometer or measuring eyepiece and the density for matching chosen for some finite value (*C120*).

WORKING CURVES

With the step sector, or other step gradient device, it is possible to use a photometer to measure mechanically the density of the chosen line pairs. From the known transmission values of the various steps it is a simple matter to determine the transmission for a uniform density of the internal standard and unknown spectrum lines, and the ratio of these logarithmic transmission values, as in the case of the smooth logarithmic wedge or sector, will give an indication of the amount of unknown in the arc or spark. In view of the linear character of the $d/\log I$ curves and the comparison of the two lines at the same blackening or density value, it is possible to set up a curve which will indicate the ratio of intensity of the two lines (known and unknown) over a considerable concentration range. This curve, known as a working curve (Fig. 5.10), forms the basis for rapid and exact quantitative analysis. If one plots the logarithm of the percentage concentration rather than percentage concentration itself, a straight line will be obtained over that particular concentration range in which extraneous factors do not interfere with the analysis.

The linear relation involved with the logarithm of the percentage composition indicates that the accuracy of the method will be a function of the amount present rather than an absolute value. In general, one can obtain results accurate within 5 per cent. of the amount present over the effective range of the working curve. The choice of concentration of the internal standard should be such as to yield a line density equivalent to the density of the unknown line at about the intermediate con-

centration value of the range over which the working curve is to be applied. The literature available on the determination of high percentage concentration of elements by this method is meager, but there appears to be no reason why a weaker spectral line of proper characteristics could not be used for the unknown element in a rather high concentration, to compare with the internal standard line, although one could not hope to increase the accuracy above 5 per cent of the total amount. In observations involving a nearly pure material it would be more to the point to determine the impurities directly and the element in high concentration by a method of difference or remainder.

Menzel has suggested that for stellar quantitative analysis as well as laboratory technique it should be possible to set up a series of curves or

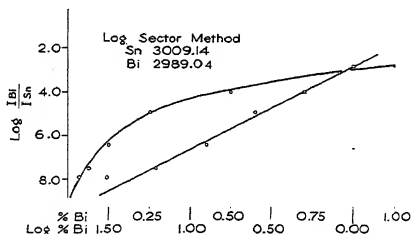


FIG. 5.10.—Working curve for analysis of bismuth, logarithmic sector method.

tables which, for certain pairs of lines of the same element but different excitation potential, should determine the excitation conditions of the source. Furthermore, it should be possible to formulate a working curve for each of these determined or assigned excitation regions so as to express the elemental concentration of the component elements in terms of a major constituent element which has been chosen as a control or internal standard. The influence of certain elements on the line intensity of other elements would, of course, be a disturbing factor which would have to be considered.

DENSITOMETER METHODS

In the above-described gradient density methods it is not necessary to consider the plate characteristics, exposure time, amount of current interruptions, development time, or many other disturbing factors. However, if these factors are carefully controlled, one may improve the accuracy of the method. If these interfering factors are sufficiently well

controlled, uniform exposures of different samples may be compared in much the same manner as the gradient intensities. In this controlled method one may compare exposures of the unknown sample with similar exposures of a series of known samples and match to an equivalent density (the method used by Meggers (C81) in his first reported quantitative analyses). If both the internal standard and unknown lines are found to be of equal intensity, no additional calibration of the plate is necessary. In the analysis of a number of samples for the same unknowns, the controlled conditions of exposure should yield internal standard lines of uniform density which may serve as a check on the constancy of exposure conditions. The series of unknown lines can thus be compared directly with a series of lines from standard samples of known composition which should be recorded on the same negative. For this comparison and assignment of elemental concentration it has been found convenient to record and plot the galvanometer swing, or blackening, of the known standard lines against the log percentage composition so as to produce a working curve, and from the galvanometer swings of the unknown lines the corresponding element percentage can be read directly.

PLATE CALIBRATION

The calibration of spectrum negatives, which is unnecessary in the use of known gradient sectors, slits, or wedges, involves the imprinting



Fig. 5.11a.—Step-density wedge (A).
Log-density wedge (B).

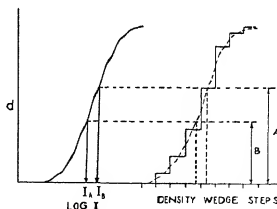


Fig. 5.11b.—Photometric measure of step density wedge pattern. Light intensities I_A and I_B will produce densities A and B as indicated on the $d/\log I$ curve and can be equated to density wedge values.

on the negative of a step wedge (Fig. 5.11a) in such a manner that the density values thus obtained cover the range over which the measurements are to be made. Since the transmission of the wedge steps is

known, the imprinted density patterns on the negative represent a negative density or blackening equivalent to a known change in light intensity. Measurement of the density of the spectrum line as compared with this series of graded densities will enable the observer to assign a definite light intensity value to the line (Fig. 5.11*b*), and hence a comparison can be made of relative intensities of spectral lines with increased accuracy. The use of a step logarithmic wedge for plate calibration will yield numerical values for density which will be proportional to the logarithm of the intensity, and the difference in these logarithmic values will be equivalent to a ratio of the line intensities in the source.

The use of a step sector or step wedge at the slit will enable the operator to impress a calibration pattern on the negative for the various spectral regions included in the plate. The calibration photograph may be made separately with a homogeneous light source, or it may be applied at the time the analysis photograph is made by the use of the unknown substance in the light source. In the determination of line density and light intensity one may determine the $d/\log I$ curve from this calibration data, or, in the use of the step wedge, slit or sector, determine the levels at which the unknown and internal standard are of equal intensity.

LINE INTENSITY—DENSITOMETERS

Densitometers may be classed as a special form of *photometer* intended for the measurement of optical density. Where the values measured are themselves a direct measure of optical intensity (e.g., photographic blackening) the resulting data may be properly called either *densitometer* or *photometer* values, and a series of values plotted in a curve may be called *densitometric* or *photometric* curves. If the densitometer or photometer is designed to measure light intensity over a limited area such as a slit or pin hole, the instrument is usually termed a *microphotometer* or *microdensitometer*.

Line intensity can be determined by means of logarithmic sector methods, by a direct measurement of the length of the spectrum line and the ratio of two line intensities by the difference in their lengths. Since the ratios of intensities are the data which are used in quantitative analysis, the length may be measured from any point common to both lines, such as a streak on the spectrum lines due to a dust spot or irregularity in the slit, or from the mark caused by the outer edge of the rotating sector. The measurement may be made with a microscope with a measuring eyepiece or a simple reading glass with a built-in scale. Such an instrument is available from the Bausch and Lomb Company in which the scale is divided into tenths of a millimeter and with which the length of

a line can be estimated to about 0.02 mm (Fig. 5.12). As another method of measurement, the negative can be enlarged either by projection or photographic enlargement and the length of line measured with a millimeter ruler.

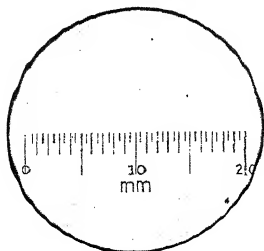


FIG. 5.12.—Measuring magnifier field (Bausch and Lomb). For reproduction purposes a 0.5-mm scale is shown. The scale supplied is in 0.1 mm divisions.

The determination of line density as a means of measurement of light intensity can be made by visual comparison and matching, although nearly always some form of photoelectric or photronic densitometer is used so as to obtain consistent results independent of the operator and more accurate than those obtained in visual matching. In principle these photronic or photoelectric densitometers (Fig. 5.13 and Fig. 5.14)

involve a steady light source of incandescent character, such as a projection bulb, connected through some type of voltage regulator, an optical

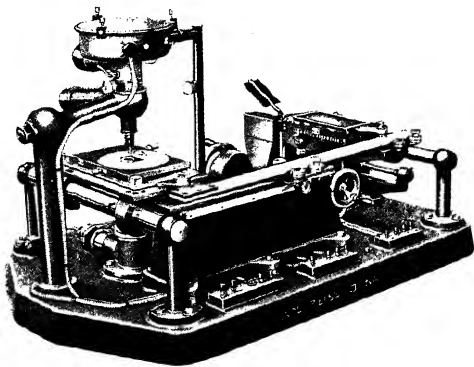


FIG. 5.13.—Recording photoelectric photometer (Zeiss).

system to illuminate the plate, and projection of the image produced on a slit in front of the photonic cell, or the focusing of the light on the plate

in the form of a line by means of a preliminary slit in front of the light source, and the illumination of the cell with this beam. The type of photronic cell, photocell, or thermopile has considerable influence on the data, and it is well to measure the density wedge itself from time to time to be sure that, over the range in which observations are made, a linear response results from various density values. It may be necessary to

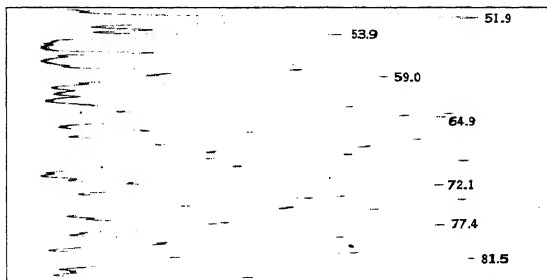


FIG. 5.14.—Microphotometer record of steel spectrum (2850 to 2885 Å), taken on a Moll (Kipp and Zonen) instrument.

calibrate the readings from the photometer in terms of the equivalent density values. Most densitometers operate through a galvanometer electrical circuit so that the density is measured by galvanometer swing. In a few instruments a null method is used with two photronic cells and a bridge balancing device so as to measure the difference between the transparent plate and the spectral line intensity.

The density of a spectrum line on a photographic plate is, by definition, a linear function, over a considerable range, of the logarithm of the light intensity which produces the latent image.

It can be shown that the amount of light transmitted by the spectrum line on the plate can be measured by the galvanometer deflection produced by the current from an interposed photronic cell, and that the deflection (D) and density (d) bear a similar relationship to the above intensity and density equation. (Deflection is defined as the difference in the galvanometer swing for a clear portion of plate as compared with the galvanometer swing for the line portion.)

$$d = c \cdot \log D$$

TABLE 5.4
WORKING CURVE DATA
Quantitative Spectrographic Analysis for Tin (Sn 3175.1)
Internal Standard Bismuth (Bi 2989.1)
(Silica-Alumina Base)

Concentrations				Logarithmic Sector Method			Densitometer Method (Clear deflection = 17.7)					
No.	Bi %	Sn %	Log Sn %	Lengths of Lines			Deflection		(I _{Bi}) Bi - 17.7	(I _{Sn}) Sn - 17.7	I _{Sn} /I _{Bi}	Log I _{Sn} /I _{Bi}
				Bi	Sn	Sn - Bi	Bi	Sn				
1	1.5
2	1.5	5.5	3.3	...	27.2	23.4
3	1.5	.031	-2.4914	5.7	4.7	-1.0	26.0	23.8	8.3	6.1	0.74	-0.1308
4	1.5	.063	-2.7993	5.2	5.3	+0.1	26.1	26.0	8.4	8.3	0.99	-0.0044
5	1.5	.125	-1.0999	5.4	7.0	+1.6	24.1	26.4	6.4	8.7	1.36	0.1335
6	1.5	.25	-1.3979	5.0	8.1	+3.1	24.2	28.6	6.5	10.9	1.68	0.2253
7	1.5	.5	-1.6990	5.0	8.9	+3.9	24.6	30.7	6.9	13.0	1.89	0.2764
8	1.5	1.0	0.0000	4.5	9.5	+5.0	24.2	30.9	6.5	13.2	2.03	0.3075

The principle of quantitative spectrographic analysis involves the intercomparison of lines of the internal standard and unknown. If d_1 and d_2 represent the densities of the standard and unknown lines then the difference in density may be equated to

$$d_1 - d_2 = \gamma \log I_1 T - \gamma \log I_2 T = \gamma \log I_1 / I_2$$

$$d_1 - d_2 = \log D_1 - \log D_2 = \log D_1 / D_2$$

hence

$$\log I_1 / I_2 = 1/\gamma \log D_1 / D_2$$

The plotting of the value $1/\gamma \log D_1 / D_2$ against the percentage composition and log percentage composition will give the required working curve for chemical analysis. In general the recording of the log deflection ratio against the log percentage composition will give a straight line whose slope will be determined by the gamma value of the photographic plate. The gamma value can be independently determined by the use of a density pattern (step or logarithmic wedge imprint on a portion of the plate) although one should realize that the gamma value is not the same for all wavelength values, usually dropping as one proceeds towards the lower-wavelength portion of the spectrum. For many forms of analysis the gamma obtained by a careful control of the illumination and development conditions is sufficiently constant so that calibration patterns are not always essential in routine work.

Plates with a high gamma will give satisfactory measurements over a

limited concentration range, whereas plates with a low gamma will cover a much wider concentration range, but with a corresponding decrease in the accuracy in the determination of the percentage concentration.

The effect of a continuous background, if small, can be corrected by the measurement of the deflection of the galvanometer for a clear portion of the spectrum adjacent to the lines to be measured, and the determination of the total line deflection by the difference between this

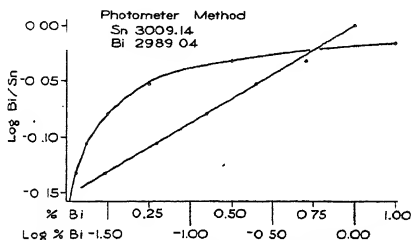


FIG. 5.15a.—Working curve. Densitometer (photometer) method.

value and that of the observed deflection for the spectrum line. Where the background is more intense it is necessary to apply an equation such as

$$d_1 - d_2 = \gamma \log (I_1 + i_1)/(I_2 + i_2)$$

in which i_1 and i_2 represent the background intensity adjacent to the two lines under observation (C125).



FIG. 5.15b.—Spectrogram for preparation of densitometer working curve. N.

In the Zeiss and the Moll instruments, devices may be incorporated to record on a photographic plate or paper the galvanometer swings in

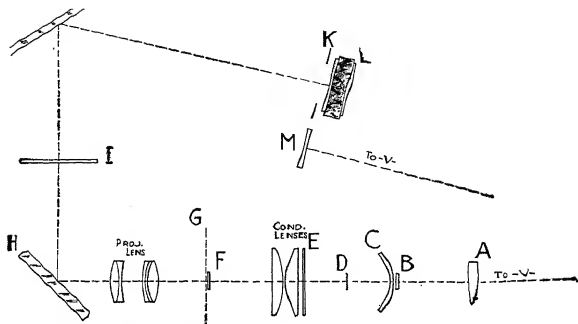


FIG. 5.16a.—Diagram of density comparator (Bausch and Lomb). Image of spectrogram negative *C* is projected onto photonic cell *L*.



FIG. 5.16b.—Density comparator (Bausch and Lomb).

the form of a microphotometer tracing. The instrument designed by Harrison for use at the Massachusetts Institute of Technology for the measurement of wavelength values includes a photoelectric device for measuring line density and recording it in the form of a moving film record.

The principal commercially available photometers for simple plate reading include those produced by Zeiss, Bausch and Lomb, and Hilger, all of which are non-recording in character (Fig. 5.16b). It is suggested that certain modifications should be incorporated in instruments for continuous analytical work; for example, an electrically operated screw should be used to move the plate along, so that the maximum swing of the galvanometer can be observed, and setting errors eliminated. For most analytical work the recording type of photometer is not at all essential since only one or two lines are to be measured and the density observed is immediately converted into some other quantitative value.

APPLICATION OF QUANTITATIVE SPECTROGRAPHIC ANALYSIS

Gouy, Watteville, Gooch, and Hart (C56) had used the spectroscope as a means of qualitative identification of potassium, but it remained for

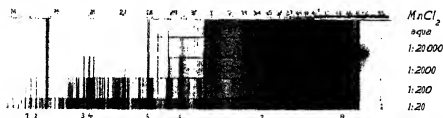


FIG. 5.17.—Portion of a spectrogram, N, from the quantitative charts in Lundegardh's "Die quantitative Spektralanalyse der Elemente" (452). Illustration shows one fourth of a chart reduced to two thirds scale.

Klemperer (C71) to indicate a quantitative relation between the intensity and analytical values. Lundegardh (452) has developed quite an extensive system of quantitative spectrum analysis through the use of a flame, arc, or spark source. In the application of his solution method Lundegardh has published data using an internal standard (quite often aluminum chloride), and measuring the line density with a thermoelectric densitometer. Some ten years later Lundegardh published a second part to his book (1934) in which he has used an immersion arc and spark holder for study of solutions, and included numerous tables of acceptable lines for analysis purposes, especially for the rare earths. The data by Lundegardh provide the best available material on quantitative flame spectra analysis.

INFLUENCE OF EXTRANEOUS ELEMENTS

A small amount of mercury produces a marked effect on the spectral intensity of neon in a discharge tube, since the spectrum of neon is practically eliminated owing to the low ionization potential of mercury and the high ionization potential of the neon atom. This effect has been noted by other workers in arc and spark spectra, and an ordered arrangement of elements has been attempted in which those above a given element would tend to decrease the spectral intensity while those below would increase the spectral intensity of the element under test. Gerlach and Schweitzer (*A18, 19*) have shown that potassium chloride could be added to a 1:1 zinc chloride-cadmium chloride solution until the solution contained 32 per cent of potassium chloride with no perceptible change in the intensity ratio of the zinc and cadmium lines. D. M. Smith (*C108*) also has pointed out that it may generally be assumed that the presence of other impurities than the one under investigation usually has no effect upon the intensity of the lines due to the unknown element. This assumption seems justified for small quantities of the extraneous elements (less than 1 per cent).

Zinc-cadmium and zinc-iron alloys which were carefully analyzed and shown to contain a variety of other elements gave satisfactory correlation in relative line intensities as compared with the standard alloys prepared especially for control and known to be free from these impurity elements. From these and other data, Smith concludes that it may be generally assumed "that the presence of other constituents than the one under consideration has no effect on the intensity of the lines due to that constituent."

On the other hand, T. Negresco (*C89*) states that in a given alloy the introduction of a third metal totally changes the sensitivity of the spectrum lines of the other two elements, and cites a copper alloy containing 10 per cent of manganese and 0.1 per cent of aluminum. In the observed spectrum the aluminum lines were practically suppressed. In this alloy, however, the manganese occurs in a comparatively large quantity, and thus apparently has a more pronounced effect than if it were present only as an additional impurity, i.e., 1 per cent or less. A similar example is the effect on cadmium lines in a zinc alloy when varying amounts of lead and iron are added.

Van Someren (*C117*) has reported the similar effects of some 10 per cent silicon in an aluminum alloy, and 10 per cent zinc in a similar alloy, both causing a lower intensity in the impurity lines and hence a lower spectrographic analysis figure as compared with the chemical analysis. As a reversal of this effect it may be pointed out that a small amount of

material, such as 0.5 per cent tin or arsenic in copper, has been reported to cause a marked increase in the density of the copper lines.

Duffendack, Wolfe, and Smith (*C46*), in comparing the intensity of barium lines in nickel and nickel-copper alloys, noted that the copper had an appreciable effect on the relative intensities of the barium lines. These examples thus confirm the general principle that due consideration must be given to the effects of each substance present on the line intensities of all the other substances present. For accurate analyses this would involve the preparation of standard or working curves with as nearly as possible the same content as the unknown, and, where more than one unknown is present in variable amounts, the working curve experimentation should include a study of the effect of the variation of each constituent on all the other constituent line intensities.

Such a series of experiments was carried out by Twyman and Hitchen (*C113*) in which they studied the influence of iron and copper on the intensities of nickel and cobalt, using chromium as the internal standard (Fig. 5.18). From these data they concluded that, although many complex factors may take part in the influence of one element on the line intensities of another, the effect is not so great but that a direct examination of the unknown substance will give the concentration of the constituents to a first approximation. A series of known standards can then be prepared and the influence of the variation of the constituents present on the line intensities of each other can easily be determined. This correction can then be applied to the original unknown analysis, or, if a series of samples are to be run, a working curve may be set up for the particular type of material under observation.

Duffendack, Wiley, and Owens (*C47*), who have further investigated this effect of one element on intensities of another, group these variations into two types: those dependent on solution characteristics, and those dependent on elemental interactions in the vapor state in the arc or spark. Sodium, potassium, and magnesium were found to decrease the line intensities of certain elements, while calcium enhanced the intensities of the potassium and magnesium with respect to cadmium.

Negative ions are known to have some effect on line intensities, and it is reported that the chloride ion increases the intensities of lines without changing the relative intensities, while sulfate and phosphate ions are reported to cause a decrease in intensities without an appreciable change in relative intensities.

Personal observations by the author have indicated that in certain substances, such as the chlorides of the alkali-earth metals, a considerable amount of the element is excited as the calcium, strontium, or barium subhalide to give the corresponding diatomic band spectra. In

fact, a method for the determination of fluorides has been reported in which the salt is mixed with calcium carbonate and arched. The intensity of the calcium fluoride band spectrum is used to determine the amount of fluoride present. Certainly a portion of the alkali-earth metals, at least in low-temperature arcs, is excited in the form of the oxide rather than the elemental state, and this would apply to the sulfate and phosphate salts which would yield oxides at the arc temperatures.

A rather important observation was made by Duffendack, Owens, et al., namely, that the influence of the extraneous element on the line intensity of the impurity, as compared with an internal standard, reached

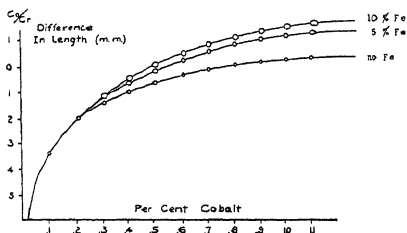


FIG. 5.18.—Influence of iron on the working curve for cobalt. Line pair Co 3405.1/Cr 3403.3. (Twyman and Hitchen [*C17*].)

a maximum value, and, by what might be termed a method of excess, i.e., addition of an excess of this extraneous element, it was possible to eliminate the necessary consideration of the effect of the extraneous element on the unknown. An excess method sometimes reduces the sensitivity of the unknown lines by slight changes in percentage composition. This was especially true of the addition of potassium in excess to an unknown containing calcium. Other workers in the field of spectroscopy have suggested the possibility of establishing an ordered arrangement of elements, much as in an electromotive series, in which the order follows the ionization potentials, with the indication that any element might have its lines depressed or enhanced by elements above or below it in the series. There appear to be numerous exceptions to this order, however, and further work seems to be necessary in this field.

Breckpot, Creffier, and Perlinghi (*C5*) have recently shown that the addition of quantities smaller than 0.3 per cent of an extraneous element to a binary system had little or no effect on the relative intensities of the

binary components, and in some instances as much as 3 per cent was added before any measurable effect could be noted.

To supply further information on this problem of influence of line intensities, Silverthorn and Brode (*C30*) have prepared a series of samples of cadmium and zinc, using in the analyses the homologous pairs of 3252.5 (Cd) and 3345.0 (Zn). The mixtures were made up in an alumina-silica base of constant composition, and to avoid chemical reaction the salts were either carbonates or sulfates but not mixtures of carbonates and sulfates. In the samples studied a mixture of 4 parts of cadmium as carbonate with 1 part of zinc as carbonate was mixed with 10 per cent of this amount of each of the following metals as carbonates: sodium, potassium, lead, magnesium, copper, and bismuth. It was found that only the last two in this concentration had an appreciable effect on the rela-

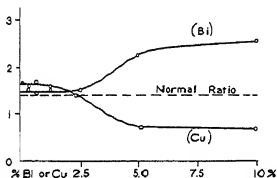


FIG. 5.19. — Influence of Bi and Cu on the Zn/Cd line ratio (carbonates) (Brode and Silverthorn [*C30*]).

tive intensity of the Cd-Zn lines, and their effects were in opposite directions. The presence of copper reduced the intensity of the Zn line as compared with the Cd line (Fig. 5.19). Bismuth, on the other hand, reduces the intensity of the Cd line as compared with the Zn line.

It has been noted that the variable effects are produced at concentrations slightly below 2 per cent of extraneous metal, and, in the samples studied, the effect becomes fairly constant above a concentration of about 5 per cent of extraneous metal. The same type of effects has been noted in studies which have been made (*C31*) on the effect of large amounts of iron on the suppression of the sensitivity of the boron lines. From these studies of extraneous-element influence on the relative intensity of line pairs it would appear that the effect is limited to certain concentration ranges and that on either side of the sensitive region the effect can be considered as constant in character. It has also been shown that the effect may be positive as well as negative with regard to the influence on line intensity.

TABLE 5.5

EFFECT OF VARIOUS AMOUNTS OF COPPER AS THE CARBONATE ON THE
Cd-Zn LINE RATIO

Composition of Samples	Line Intensity		
	Cd (3252.5)	Zn (3345.0)	Difference
1. Cd-Zn mixture	8.1	9.5	1.4
2. Cd-Zn mixture + 10 % Cu	8.1	8.8	0.7
3. Cd-Zn mixture + 5 % Cu	8.5	9.2	0.7
4. Cd-Zn mixture + 2.5 % Cu	7.6	9.0	1.4
5. Cd-Zn mixture + 1.25 % Cu	8.0	9.6	1.6
6. Cd-Zn mixture + 0.625% Cu	7.7	9.4	1.7
7. Cd-Zn mixture + 0.312% Cu	7.5	9.0	1.5
8. Cd-Zn mixture + 0.156% Cu	7.0	8.6	1.6

CHOICE OF INTERNAL STANDARDS

For complete quantitative analyses it is recommended that working curves be prepared in which the extraneous elements are in equivalent quantity to that of the unknown series, and, where some doubt exists as to their effect, a set of working curves should be prepared with different concentrations of the extraneous elements. It is therefore impossible to publish satisfactory working curves for general application although each individual worker can rely on them for the particular problem for which he has prepared the proper standard series. The spectrographic analyst can be assisted, however, by the publication of lists of pairs of lines which are known to furnish satisfactory data for analytical working curves. Lundegardh (*A52*) and Gerlach (*A19*) have published such lists.

Other methods which have been suggested for the intensity determination of lines in an emission spectrum include the direct measurement of line intensity by means of a monochromator and photoelectric cell system, and the use of a moving plate on a known amount of sample in a controlled arc so as to measure the duration of the line in the arc. Neither of these methods is integrating in character, as is the photographic plate, and therefore they depend on sufficient intensity of the line to affect the cell or the momentary exposure which is given to the plate.

One might classify the methods of quantitative analysis as follows: (1) the length of lines in the spark discharge, (2) the number of lines recorded on a plate after a controlled exposure, (3) the intensity of lines on

a plate (Figs. 5.20 and 5.21), (4) the time for disappearance of lines in a standard arc, and (5) the direct photoelectric determination of line in-

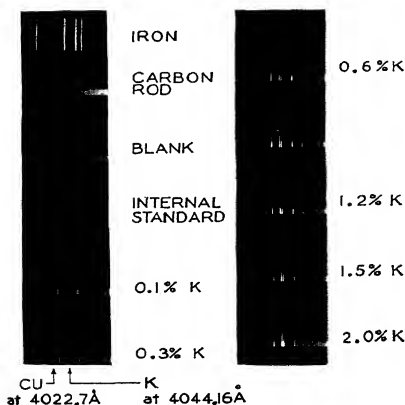


FIG. 5.20.—Standard spectra for determination of working curve for potassium in leaf materials (Cu internal standard) (Brode and Wander [C.33]). P.

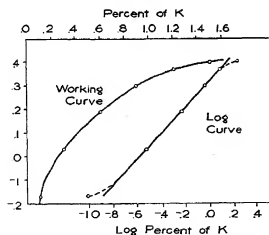


FIG. 5.21.—Working curve for potassium. K 4044.1 Cu 4022.7. (Brode and Wander [C.33]). Ordinate indicates difference in line length.

tensity by means of a monochromator. Of the various methods the second (number of lines on a plate [Hartley]) is the earliest. The most successful results have involved the third method (intensity of lines on the plate).

SPECIAL NOTE

Users of spectrographic methods of analysis, including those engaged in non-profit research as well as those working upon commercial applications, should be cognizant of the existence of U. S. Patent 1,979,964 (application made March 14, 1932, and granted Nov. 6, 1934 (*C44*).) The claims include the following:

1. The method of quantitative spectroscopic analysis which comprises the following steps: establishing an arc current between electrodes comprising the unknown material of a value such that the intensity of spectral lines does not vary materially with unavoidable fluctuations in arc current, recording the spectrum of the arc, measuring the ratio of intensities of a pair of lines in the spectrum by comparison of the strengths of the corresponding recorded lines, repeating the process with a series of electrodes containing the same kind of material but of known analysis, making use of the same spectral lines, evaluating the ratio of intensities obtained from the unknown material in terms of percentage of an element producing one of the lines by comparing the ratio of intensity of the unknown with the ratio of intensity of said known specimens.

In following claims the use of a spark and luminous discharge are covered as well as the recording of the spectrum on a photographic plate. In view of the large amount of previously published work in the field of spectrographic quantitative analysis, much of which is referred to in the patent, it seems unfortunate that a patent claim should be granted which rather effectively covers the fundamental principles involved in this analytical field. (See also U. S. Patent 2,043,053.)

LITERATURE

General and Reference

"Chemische Spektralanalyse." G. Scheibe (*A59*).

"Chemical Analysis by Emission Spectra." 3 Volumes. W. Gerlach and others (*A18*) (*A19*).

"Chemische Spektralanalyse." W. Seith and K. Ruthardt (*A62*).

"A Course in Chemical Spectroscopy." H. W. Thompson (*A69*).

"Die quantitative Spektralanalyse der Elemente." H. Lundegardh (*A52*).

"Metallurgical Analysis by the Spectrograph." D. M. Smith (*A63*).

CHAPTER VI

RESONANCE AND CHEMICAL STRUCTURE (*B22, B44*)

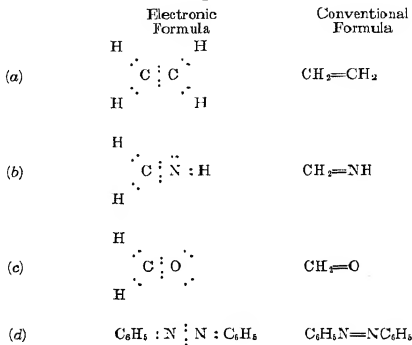
Compared with the simpler di-, tri-, and symmetrical polyatomic compounds described in Chapter II (p. 22), the more complicated unsymmetrical absorbing molecules produce a very complex resonance and spectrum. It is difficult to set up exact limitations, for rules and effects which may apply in one case may not in another. With the exception of certain colored ions it is usual to have a number of atoms together, rather than a single atom, as the nucleus or resonating system. This nucleus of resonating atoms is known as the *chromophore* of the molecule, and a molecule containing such a group of atoms is known as a *chromogen*. The shift of an absorption band as a result of some external action on the chromophore is termed a *hypsochromic* effect if it involves a shift to higher frequency values and a *bathochromic* effect if it involves a shift to lower frequency values.

It is sometimes difficult to define precisely the size or sphere of influence of a chromophore, especially when the molecule contains a large number of similar atoms, as do the organic compounds. All atomic linkages such as C—H or O—H will have resonating properties and will produce absorption spectra, but these simpler linkages produce effects which are to be found only in infrared, Raman, and extreme ultraviolet spectra (see section on infrared spectra). Within the visible, the near infrared, and the photographically available region of the ultraviolet, the simplest absorbing or resonating groups all seem to involve two or more atoms coupled together by the sharing of four rather than two electrons. The commonly known chromophores include $C=C$, $C=N$, $C=O$, $N=O$, $N=N$, $C=S$, etc. In such groups (Fig. 6.1a) it is to be noted that there is apparently an outer satisfied shell surrounding the entire unit of the two carbon atoms, but that within the completed shell there is a condition which the organic chemist terms unsaturation. The molecule is capable of absorbing additive substances such as H_2 , Br_2 , H_2SO_4 , etc. This unsaturated or resonating nucleus, as Pauling has shown, is capable of vibrating in certain predetermined resonating systems.

To appreciate more fully the conditions involved in molecular vibration and absorption it is essential to consider the nature of the binding between atoms. The atoms constituting a molecule may be held together

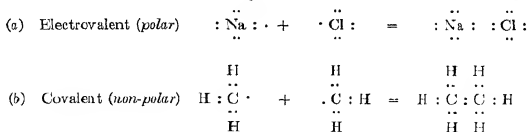
by either electrovalent or covalent forces. Polar or electrovalent combination is the result of a complete transfer of an electron from one atom to another, and the binding or holding force results from the electrostatic forces of the oppositely charged ions. Non-polar or covalent com-

Fig. 6.1



bination is the result of sharing of electrons so that they are common to the outer shells of both atoms (Fig. 6.2). The sharing of electrons to form covalent structures may involve two, four, or six electrons, but there is no evidence for the sharing of an odd number of electrons such as one or three (C92).

Fig. 6.2



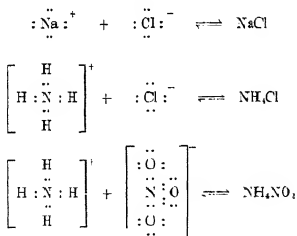
Electrovalence is of little importance with regard to the color of the molecule or resonance between atoms since this ionic binding tends to separate the two parts into complete shells which are not rigidly held in a definite orientation. Covalent bonds, on the other hand, involve the direct binding in fixed orientation of the atoms and the ability to resonate or vibrate as a unit. Electrovalent structures may result in a change in

the color through an alteration of the covalent forces of one of the atoms involved in both electrovalent and covalent combination.

COVALENT BONDS

Covalent structures may result either from the furnishing of one electron by each of the atoms to form a pair which is shared by both shells to yield a completed octet, this covalent structure being known as the normal type; or covalent structures may be formed by the donation of two electrons of one atom to another atom with six electrons to result in completed outer octet shells. This latter type of covalence is termed a coordinated bond or valence, the two atoms being designated the donor atom and the acceptor atom. In the combination of halogen acids with ammonia one finds examples of the covalent and electronic binding in which the hydrogen is coordinately bound to the nitrogen. Definite rules can be established governing the valence relations in molecular formation. Ionic valence may take place between two atoms, two radicals, or an atom and a radical (Fig. 6.3). It should be noted in the case of ionic valence involving radicals that it is the radical as a whole, and not any one atom, which has the electrical charge and acts as the individual element.

Fig. 6.3



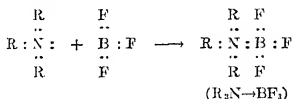
Covalent bonds, as has been indicated, may exist either as the normal covalent link or the coordinated link (depending on whether one or both of the shared electrons come from the donor atom). If both the shared electrons come from the donor atom the resulting compound will consist of two parts, in one of which (the acceptor) the positive charge will be decreased, and in the other (the donor) the positive charge will be increased. If only one electron comes from the donor atom there will be no

change in the charges in the two atoms and a true covalent bond is said to exist. Coordinated valence is thus partly covalent and partly ionic in character, one of the shared electrons being considered as covalent and the second as ionic. The latter bond is sometimes referred to as an intramolecular ion (*zwitterion*), and the binding of the two atoms as semi-polar.

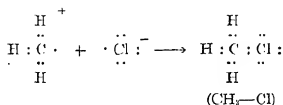
Examples of coordination and covalence are furnished by the combination of NR_3 with BF_3 , and $\text{CH}_3^+ +$ with Cl^- (Fig. 6.4). The arrow serves to indicate the electron shift from the donor to the acceptor atom ($\text{A} \rightarrow \text{B}$), sometimes indicated in the literature by $+$ and $-$ for donor and acceptor, respectively ($\bar{\text{A}} - \bar{\text{B}}$).

Fig. 6.4
Covalent Bonds

(a) Coordinate Bond



(b) Normal Covalent Bond



RESONATING STRUCTURES

When the electronic structure of a compound can exist in two or more forms of nearly equal energy content, resonance is possible and the relative stability of the two forms will determine the distribution in the equilibrium mixture. Resonance involves the same molecular structure with only a shift in the electronic distribution and should not be confused with tautomerism or dynamic isomerism which involves the equilibrium between compounds of the same molecular formula but different atomic distribution (Fig. 6.5).

The various resonance forms arising from this dynamic electronic effect are known as *electromers*, just as the forms arising from dynamic isomerism (tautomerism) are known as *tautomers*. The electromers may be indicated as the neutral and active forms, the neutral ones usually being indicated by the simple bond formulas and the active ones requiring

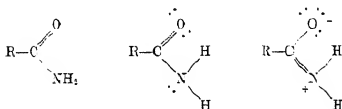
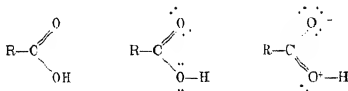
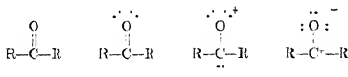
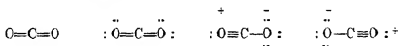
electronic or charge indications. In the single sharing of electrons as in $R-OH$, the oxygen may act as donor group transmitting an additional electron pair to the C or the R group and thus forcing a redistribution of electron concentration in the R radical. In phenol, the distribution will

Fig. 6.5

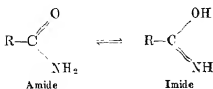
Electromeric Formulas

Resonating Structures

(Note: shared pairs of electrons are indicated by bonds;
 $+$ and $-$ indicate electron gain or loss.)



Tautomeric Formulas



result in a concentration of electrons at the ortho and para positions and thus activate these positions towards groups capable of receiving electrons.

There are, of course, many ways in which the above effects may be indicated. Another method of presentation involves the electron spacing

TABLE 6.1

RESIDUAL SINGLE BOND ENERGIES (VOLT-ELECTRONS) AND REFRACTION CONSTANTS

Bond	Energy	Refraction
H→C	4.32	1.70
H→N	3.89	1.80
H→O	4.75	1.85
H→Cl	4.38	6.67
H→Br	3.74	9.14
C→C	3.65	1.21
C→N	2.95	1.55
C→O	3.55	1.43
C→Cl	3.41	6.57

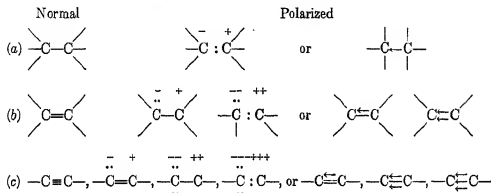
in the molecule. It may be assumed that in the normal or neutral state the electron pair occupies an intermediate position between the sharing atoms, A : B, but that the active position would involve the shift of the electron pair, e.g., A: B or A :B. Increasing electron concentration on A will induce electron release more readily on those atoms alternate (ortho) to A. It has been possible through a study of chemical data to calculate the electron distribution between various covalent linkages, the energy, and the refractive index factors for simple coordinated diatomic structures. Reasonably good results are obtained in the prediction of refractive index values from the additive effects of these components (Table 6.1), but it must be remembered that these are for a limited number of wavelength values. There is a close tie between refractive index and absorption spectrum, and it would be expected that any such system of prediction which would permit the indication of refractive index for various wavelength values would also serve to predict the absorption spectra of the compound.

An important point to note in this discussion is that electrons in their rearrangement shifts to form electromers move in pairs, and there is no good evidence for the existence of electromers involving sharing of one or three electrons. Single bonds will thus indicate the sharing of two electrons, double bonds the sharing of four electrons, and triple bonds the sharing of six electrons. Compounds involving the sharing of four or six electrons (double and triple bonds) will have these sharing atoms closer together than the corresponding linkage involving the sharing of only two electrons (single bond). Single bond coupling, especially be-

tween like atoms such as the C—C linkage (a), will be less readily polarized than the corresponding double bond, C=C (b), and triple bond, C≡C linkages (c). In the three examples mentioned, the normal and active or polarized structures may be indicated as:

Fig. 6.6

Normal and polarized structures



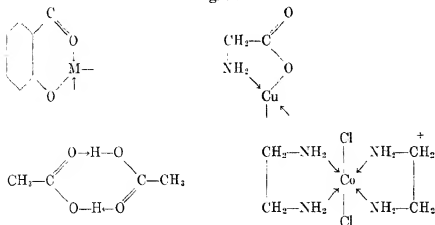
or using a bond (—) for shared electrons and only indicating unshared electrons, (c) becomes:



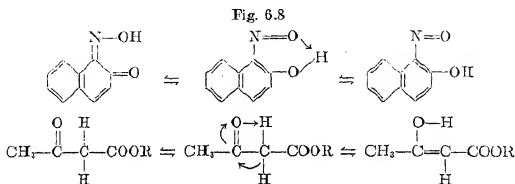
CHELATE RINGS

The ability of neutral molecules to donate electrons results in the formation of coordination compounds which are neutral stable structures. This coordination may involve two parts of one molecule reacting together, or the combination of a donor and acceptor molecule. In those cases where the two parts (donor and acceptor) of the same molecule react together, or there is an interaction between two molecules, each of which contains a pair of donor and acceptor electrons, there will be formed a ring structure which is known as a chelate form (Fig. 6.7).

Fig. 6.7



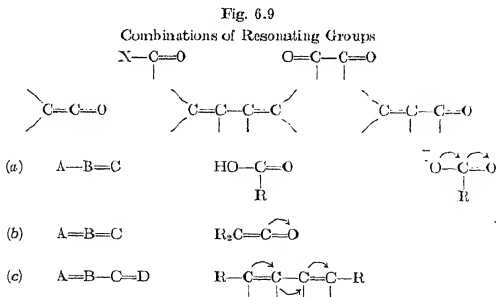
In so far as chelation is involved with a hydrogen atom we may term the effect a hydrogen bridge. The hydrogen bridge may thus represent the intermediate point in the migration of a hydrogen atom and the equilibrium shift in such a tautomeric equilibrium as the enol-keto tautomerism or benzenoid-quinoid equilibrium (Fig. 6.8).



The salts of such enol forms may be ionized in the normal way, or, in the case of coordinating properties of the metal salt-forming group, a chelate structure may be produced.

MULTIPLE RESONATORS

The combination of two or more resonating groups may result in an increase or decrease in the activity of the entire system. In general, there is an increase in activity when the resonating groups are separated by a single bond connection as in Fig. 6.9, and an active or polarized form of the neutral molecule will possess two opposite groups at the ends and a neutral portion in the center.



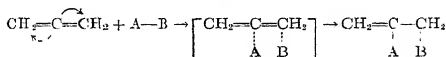
In the simplest type of polyfunctional electromeric system involving two resonating systems, the structural and resonating formulas may be

indicated as $A-B=C$ (Fig. 6.9). The ease with which the donor atom or group releases its electrons will determine the degree of equilibrium between the polar and normal form. In a comparison of a series of related $A-B=C$ cases such as the above formulas, it is evident that in the acid (a) little if any carbonyl structure is present, while in a ketone the carbonyl structure is predominant.

CUMULATIVE RESONATORS

In those compounds containing two resonating systems each of which is produced by a double bond, the simple allene may be indicated as the resonating structure $A=B=C$.

Fig. 6.10

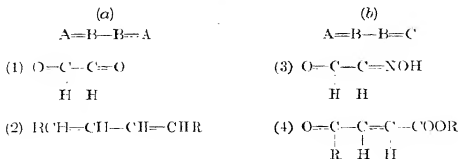


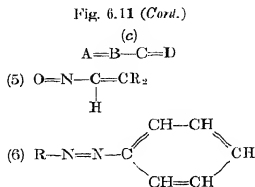
Since only one of the two resonating groups is activated, addition will take place either 1,2 or 2,3 but not 1,3 (Fig. 6.10). Other examples of this type include ketenes in which the oxygen acts as an acceptor from the carbon and in turn as a donor to a reacting substance which adds to the oxygen and adjacent carbon. In general, it may be said that similar resonating groups attached to the same atom neutralize, in part, rather than amplify the resonance of the molecule.

CONJUGATED RESONATORS

When two or more resonating systems are joined by a simple covalent linkage involving the sharing of two electrons, the resonators are said to be conjugated together. The simplest examples, $A=B-B=A$, involve like groups, although the same effects are noted in mixed systems such as $A=B-B=C$. The following are examples of such resonating compounds:

Fig. 6.11





The conjugated compounds generally show a marked increase in resonance and activity over that which would be predicted from the sum of the component resonators.

The resonance energies for some of the conjugated systems (Table 6.2) indicate an increase in energy which is greater than the increase in

TABLE 6.2
RESONANCE ENERGIES OF CONJUGATED SYSTEMS
(Pauling and Sherman) (*C98*)

1,3-Dienes	8.0	Fulvene	15.0	Naphthalene	74.7
1,3,5-Trienes	16.7	Benzene	37.3	Pyridine	43.1
1,3,5,7-Tetrenes	25.1	Stilbene	94.3	Furan	21.4

similar nonconjugated resonating groups. By comparison of properties it is to be noted that the 1,3 (conjugated) dienes (double bond or resonating groups) are different from the 1,2 and 1,4 dienes in which the double bonds are not conjugated together. The 1,5 diene shows essentially the same properties as the two monoolefins it would form if it were split apart at the third position. Benzene may be considered as a conjugated ring, and much of its stability is ascribed to the alternate double bond—single bond structure.

Unsaturated ketones of the formula $R''-C(=C-CH_3)-C(=O)-R'$ belong to

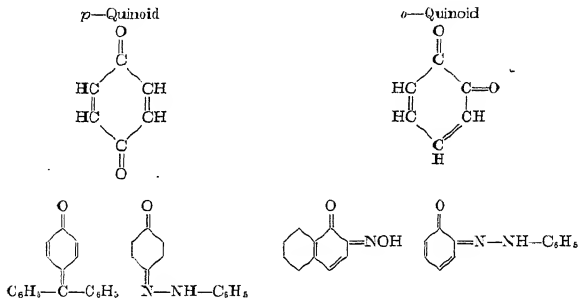


the same type of resonating systems, especially when some resonating group occupies the R' position. Such groups as H or CH_3 inhibit the 1,4 addition reaction which is characteristic of conjugated unsaturation, but resonating groups such as C_6H_5 , OR, and NR_2 markedly increase the yield when occupying the R' position and inhibit the reaction when in the R'' position.

As a color-producing and absorbing system, the conjugated systems involved in 1,2 diketones and 1,4 unsaturated diketones are of great importance. In aromatic compounds these are represented as the ortho and para quinoid resonators (Fig. 6.12).

In the quinoid structures one notes the same effects as in the 1,3 conjugated unsaturated compounds previously described. Acceptor groups such as $\text{H}-$ and CH_3- induce activity and resonance when attached to the center of the resonator, whereas $\text{OR}-$ groups (donor) reduce activity and inhibit resonance of the quinoid structure. The $-\text{OH}$ and $-\text{NH}_2$ radicals and their derivatives, because of their marked influence on the resonance of a system, when attached in the proper position have been termed *auxochromes*, or color-enhancing groups. The colored forms of

Fig. 6.12
Quinoid Structures



nearly all aromatic dyestuffs can be indicated by resonance between certain quinoid and chromophoric forms. The activation of the *ortho* and *para* positions of aromatic compounds through the presence of these groups is another demonstration of this conjugated activity enhancement. On the other hand, such radicals as $-\text{NO}$ or $-\text{NO}_2$ activate *meta* positions in an aromatic nucleus, since they are the opposite in electronic properties from the $-\text{OH}$ or $-\text{NH}_2$ radicals.

FREE RADICALS

One other form of resonating system, known as a free radical, should be considered. A free radical, such as the triphenylmethyl, $(\text{C}_6\text{H}_5)_3\text{C}\cdot$, violates the accepted chemical principle of even-numbered electrons or shared pairs in a substance capable of separate existence. As might be expected, these radicals are not very stable, and as acceptors they appear to be highly unsaturated molecules. The negative character of the aryl radicals in part offsets the lack of a negative charge sufficient to satisfy the positive proton charge so that the triphenylmethyl chloride is ca-

pable of ionization to yield a colored anion. The free radical produced from the triaryl compound is also colored, although not so deeply. The singlet electron in the free radical is distributed over the entire system through the effect which may still be termed resonance. The colored ion represents a positively charged body in which there is a corresponding deficiency of one electron in the outer shell. Like the free radical, this anion has a surrounding group of negative aryl radicals, and there is a tendency to the formation of a resonating system and the corresponding absorption of energy or the production of color, it being an experimentally observed fact that resonating systems absorb more energy than would be normally predicted from the sum of the vibrational energy of their various component units.

LITERATURE

General and Reference

"Modern Electronic Concepts of Valence." J. R. Johnson (*B22*)

"The Significance of Resonance to the Nature of the Chemical Bond and the Structure of Molecules," L. Pauling (*B44*).

"Modern Theories of Organic Chemistry." H. B. Watson (*B58*).

CHAPTER VII

ABSORPTION SPECTRA

ANALYSIS OF SPECTRA OF COMPLEX MOLECULES

The complexity of diatomic spectral analysis becomes, in appearance, very simple when one attempts any exact mathematical analysis of the more complex molecules. A few triatomic and higher molecules of symmetrical nature, such as carbon dioxide, carbon disulfide, formaldehyde, and phosgene, have yielded to some degree of analysis (Fig. 7.1), but the

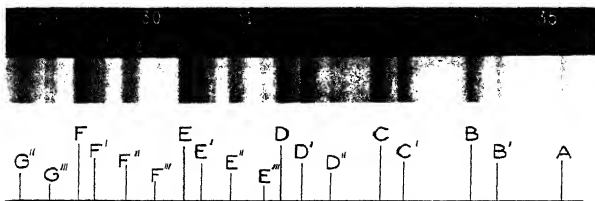


FIG. 7.1.—Band spectrum of formaldehyde vapor, P, (after Henri and Schou [C68]).

very symmetrical benzene molecule, although it gives a remarkably well-defined absorption spectrum in the vapor state (Fig. 7.2a-A), has not yielded to a satisfactory interpretation of its spectrum. It seems quite apparent from a study of the absorption spectra of many of the highly complicated molecules that there is a transition from what one might call the atomic-electronic spectrum to a true molecular spectrum involving a resonance or vibration of the molecule as a whole. In these larger molecules the resonator or vibrator appears to act in accordance with the general laws involving harmonic vibration such as might be applied to resonators, strings, reeds, or other mechanically vibrating bodies. It must be admitted, however, that there is no sharp dividing line between atomic and molecular vibration as indicated, but for highly complex organic and inorganic resonators there is considerable value in a harmonic resonating theory. The nature of most molecular compounds precludes emission spectra, so that our discussion in this field will be confined to absorption spectra.

The recording of absorption spectra of complex molecules on a frequency scale will, in general, show a simple relation between the bands if

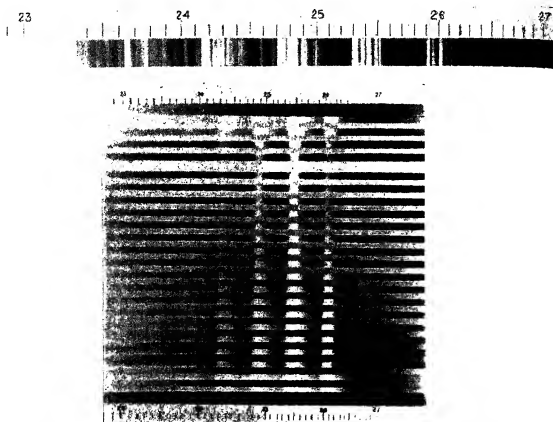


FIG. 7.2a.—Band spectra of benzene, *A* vapor (upper) *N*, *B* solution in alcohol (lower) *N*.

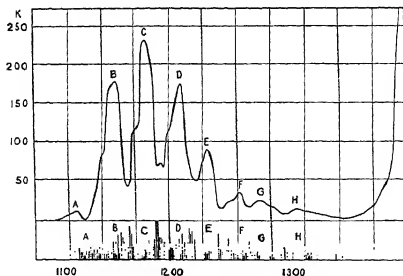


FIG. 7.2b.—Graphical analysis of solution (upper) and vapor (lower) spectra of benzene.

two or more are present. The seven bands of benzene (Fig. 7.2) show a uniform separation so that they could be considered as harmonics of a

fundamental vibration of 30.2 f. The difference between the absorption spectra of benzene in the gaseous state and in solution is largely due to the modifying and dampening effects of the solution which, because of

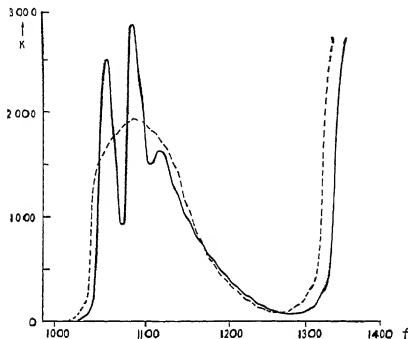


FIG. 7.3.—Influence of solvents on absorption bands. Absorption spectra of phenol in alcohol (---) and in hexane (—). (Klingstedt [C72].)

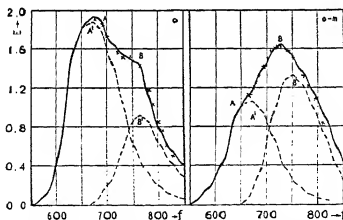


FIG. 7.4a.—The analysis of observed absorption bands into component curves.

The above curves represent the absorption spectra of phenylazo-*o*-cresol (*o*), and *o*-tolylazo-*m*-cresol (*o-m*) in a 3 per cent aqueous solution of sodium hydroxide. The *x* marks on the graphs indicate values obtained from the addition of the component bands *A'* and *B'*. (Brode [C13].)

close proximity of the molecules, prevent an unhindered vibration so that the average position of vibration will be recorded with a decrease on each side of this position. This averaging effect is more marked in polar than in non-polar solvents (Fig. 7.3), such as alcohol and hexane.

TABLE 7.1

ANALYSIS OF THE ABSORPTION SPECTRA OF THE COBALT HALIDES IN THE CORRESPONDING CONCENTRATED HALOGEN ACIDS, AS BASED ON A CONSTANT DIFFERENCE (Brode and Morton [C8, C28])

Multiple or Band Number	Cobalt Chloride		Cobalt Bromide		Comparison† between Chloride and Bromide Systems (Band Intensity)		Cobalt Iodide
	Frequency Differ- ence of 12.28		Frequency Differ- ence of 11.7				Frequency Difference of 10.79
	Calcu- lated	Ob- served	Calcu- lated	Ob- served	Bro- mide	Chlo- ride	Observed
<i>a</i> 35	430	432	409	408†	+sss	+sss	377
<i>b</i> 36	442	442	421	418†	+ss	+ss	388
<i>c</i> 37	454	450	433	430†	+sss	+sss	399
<i>d</i> 38	467	465	444	442†	+ss	+ss	410
<i>e</i> 39	479	478	456	455†	+ss	+ss	420
<i>f</i> 40	491	491	468	465†	+ss	+ss	431
<i>g</i> 41	503	505	479	476†	+s	+s	—
42	515	—	491	492†	+	+	—
43	527	—	503	501	+	—?	—
44	540	543	514	516	+	+	—
45	552	—	526	—*	—	—	—
46	565	561	538	535	+s	+ss	—
47	577	—	549	—*	—	—	—
48	589	593	561	561	+ss	+s	—
49	602	—	573	—*	—	—	—
50	614	610	584	—*	—	—	—
51	626	—	596	—*	—	—	—
52	638	?	608	610	+	?	—
53	651	—	619	—*	—	—	—
54	662	664	631	631	+ss	+s	—
55	675	677	643	649	+ss	+s	—
56	688	—	654	—	?	—	—
57	700	704	666	664	+	+	—
58	712	—	678	—*	—	—	—
59	724	—	690	690	+s	—	—
60	735	—	701	—*	—	—	—
61	747	—	713	714	+s	—	—

* It will be noticed that from multiples 35 to 42 the sequence of component bands is uninterrupted, whereas from multiples 43 to 61 about half the components are missing. The failure to detect these bands may lessen the cogency of the conclusion that all the bands fall into one series, but the absence of the same multiples in both the chloride and bromide series tends to counterbalance this weakness in the argument.

† Based on analysis in Fig. 7.4*b*.

‡ Relative intensity as compared to adjacent bands is indicated by s, ss, or sss. + indicates apparent presence as indicated by a maximum or inflection in the absorption curve. — indicates apparent absence or no indication of a maximum or inflection.

The averaging effect produced by solution interference and molecular irregularity, in reality, results in a simplification of the spectral data, although the band widths are such as to overlap in nearly all cases. The overlapping of bands does not always prevent a reasonably accurate analysis of the component structures and application of the data. The

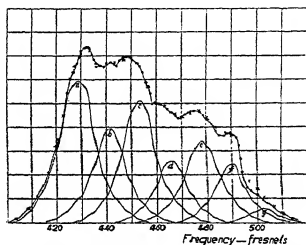


FIG. 7.4b.—Absorption spectrum of cobalt chloride in concentrated hydrochloric acid and its analysis into component bands (Brode [C8]). o = Observed; x = Calculated. complex band of cobalt chloride, in concentrated hydrochloric acid as a solvent, has been shown to consist of a number of component parts (C8, C28) (Fig. 7.4b) and has been resolved into its component structure.

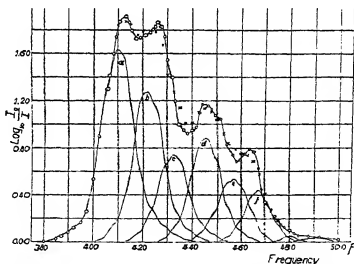


FIG. 7.4c.—Absorption spectrum of cobalt bromide in concentrated hydrobromic acid and its analysis into component bands (Brode and Morton [C28]). o = Observed; x = Calculated.

It can be shown that there is a uniform frequency separation of 12.28 f between adjacent members, and further, that the frequency of each component is a multiple of this frequency of separation (Table 7.1). As an

expansion of the system, more concentrated solutions of cobalt chloride were examined with an extension of the multiple frequency spacing to the fifty-seventh harmonic. A further examination of the bromo and iodo derivatives of cobalt in their corresponding concentrated halogen acid solutions revealed a similar system with multiple frequency differences. The differences were lower in accordance with an increase of molecular weight of the halogen complex (Table 7.1), but the multiple values for the first and the intense bands remained the same. All these separate smaller bands may thus be considered as the components of

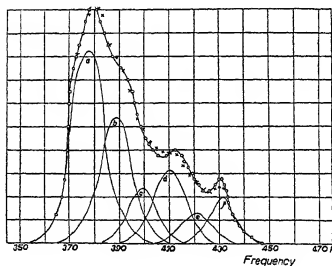


Fig. 7.4d.—Absorption spectrum of cobalt iodide in concentrated hydroiodic acid and its analysis into component bands (Brode and Morton [*C 28*]). o = Observed; x = Calculated.

larger bands, and these larger bands in turn possess multiple relations with other principal bands.

WEIGHTING EFFECTS IN RARE EARTH AND INORGANIC COMPOUNDS

Although there is a marked similarity in the spectra of the rare earths and other inorganic materials such as the cobalt salts, the absorption spectra of the rare-earth compounds deserve separate consideration. From a study of the electron assignments of the atoms it is to be noted that the rare earths possess an incompleated $4f$ group in the N shell while possessing at the same time completed $5s$ and $5p$ electron groups in the O shell and the same outer configuration in the P shell. As might be predicted, the absorption bands of the rare earths undergo considerable narrowing and sharpening as the temperature is lowered so that at liquid-air temperatures the bands may be less than an angstrom in width (Fig. 7.5). At low temperatures the atom does not exist in higher states than the ground state, and hence some of the lines will disappear. The continuance of absorption at low temperatures gives some indica-

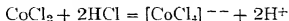
tion that the absorption is due to the atom rather than the molecule, except that the change of molecular composition, as is also true of other organic and inorganic molecules, results in a shift of the absorption bands, although this shift is not so pronounced at low as at high temperatures. Although there is some evidence that the absorption bands of the rare earths originate in the atom, it is also apparent that the bands are influenced by the atoms in combination with the rare earth, and the same effect is apparent in other inorganic color-producing elements. In the rare earths, the incompleated shell is well within the atom and protected from some of the surrounding influences by additional electron shells. The color, or light absorption, produced involves a transition from a higher level to this incomplete level. The addition of certain protecting groups



FIG. 7.5.—Absorption spectra of praseodymium acetate at room temperature (top) and liquid-air temperature (bottom). Neon spectrum in middle. P.

around the atom in the form of anions serves further to protect and to prevent the external disturbance of the resonance or electron shifts. At lower temperatures, additional protection is afforded in the reduction of molecular vibration, and hence sharpening of the bands, since the energy jumps will become more uniform and constant with a reduction of the outside disturbing factors.

If outside disturbing forces could be minimized, it would be expected that nearly line-like components of the band structure would be resolved in the spectrum. Cobalt chloride in concentrated hydrochloric acid is an example of this type. There is an apparent reaction of



the cobalt being completely surrounded by the four chlorine atoms and the whole molecule acting as a single vibrating unit, in which the incomplete shell is buried within the molecule in the *M* or *N* shell. In a solvent consisting essentially of Cl^- and H^+ ions this tetrahalogen compound is quite free from outside influences and exhibits well-defined band structure (Fig. 7.4b).

The change of the external mass or protecting shell of the vibrating nucleus without altering the mass of the inner atom produces quite a different effect from that produced in going from one member to another in the rare earth series, where the inner mass is altered without changing

the electron configuration or weighting beyond the partially filled shell. The changes in the spectrum resulting from addition outside the chromophore, or vibrating nucleus, rather than from changes within, may be classified as (a) changes in frequency, and (b) changes in intensity. From simple mechanical principles it would be expected that the mere weighting of a vibrating body would decrease the frequency with which the vibrating body oscillates (Fig. 7.6). The change in frequency of an absorption band towards lower values as the result of the addition of some weighting group, without the change in the spectral appearance, is evidence that the added group is directly connected to the vibrating nucleus and actually forms a part of the vibrating body.

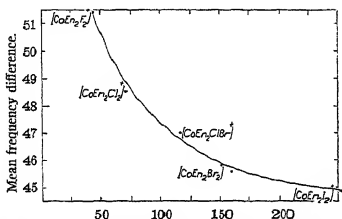
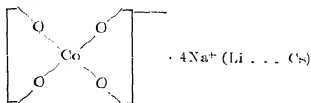
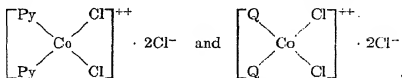


FIG. 7.6.—Change of frequency difference between component bands, in the 1,6 series of $(\text{CoEn}_2\text{X}_2)\text{X}$, caused by a change of halogen substituent (Brode and Ernberger [C22]).

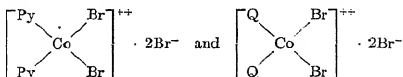
It does not necessarily follow that all elements or radicals transmit their weighting effects to the nucleus to which they may be attached. There are many groups such as the methylene ($-\text{CH}_2-$) which act as a cushion or shock absorber by failing to transmit vibration from one part of the molecule to another, whereas an ethenylene linkage ($-\text{CH}=\text{CH}-$) not only transmits vibrational effects, but, in many cases, acts as a resonating or amplifying system to enhance the spectrum intensity. Such elements as oxygen, nitrogen, and sulfur often act as weighting elements in themselves, but the effects of groups attached to them are not transmitted. Examples of this type are shown in the lithium, sodium, potassium, rubidium, and cesium, series of cobalt glasses where the chromophoric complex is accepted as



and where the change in the metal from lithium to cesium does not appreciably effect the frequency of the vibrating system. A substitution, however, of sulfur for oxygen causes a marked shift to lower frequency (*C15*). A similar case is that of the cobalt pyridinium and quinolinium halides in which the absorption bands of the two salts



(Fig. 7.7) have approximately the same frequency, whereas the introduction of bromine in place of chlorine in each of these compounds to produce



result in a weighting shift since the halogens are directly attached to the cobalt, whereas the additional carbon and hydrogen atoms in quinoline are attached through the nitrogen and not directly to the cobalt.

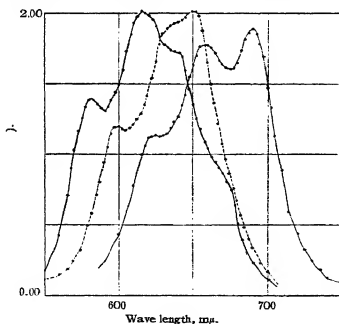


Fig. 7.7.—The absorption spectra of cobaltous halides in quinoline; —, CoCl_2 ; ----, CoBr_2 ; — · —, CoI_2 . Nearly identical curves were obtained from cobalt quinolinium halides in quinoline and cobalt halides and cobalt pyridinium halides in pyridine. (Brode [*C16*].)

The second (b) type of effect resulting from the change of exterior weighting of a chromophore involves the relative intensities of the bands which are components of the absorption spectrum. This effect is involved in relative intensities of components and is apparently more a function

of electronic forces than of mass, the greatest effects being observed in those compounds which have their nuclei or conjugated center at a greater distance from the chromophoric center. In comparing the absorption spectra of the cobalt halides (Fig. 7.4) it is to be noted that, in addition to the shift of frequency due to a weighting effect, there is also an enhancing effect involving a concentration of the major intensity in the first component of the series of bands. The same effect is to be

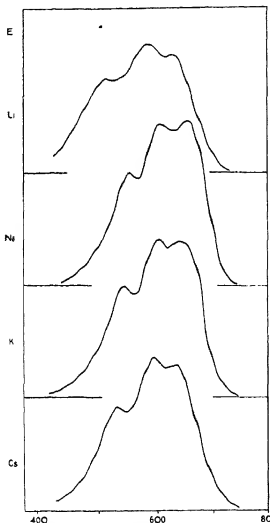


FIG. 7.8.—Absorption spectra of cobalt oxide in lithium oxide-, sodium oxide-, potassium oxide-, and cesium oxide-boric oxide glasses. (Brode [C15].)

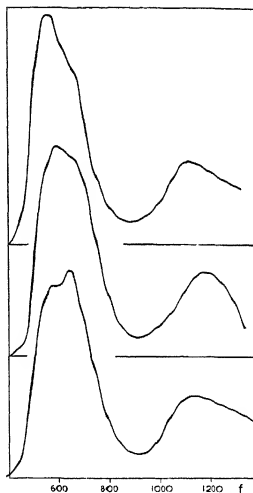


FIG. 7.9.—Absorption of *o*, *m'*, and *m*-methylphenylazophenol in 3 per cent NaOH solution. (Brode [C13].)








noted in the derivatives of benzeneazophenol (C9) (Fig. 7.9) in which a shift of a methyl, nitro, or halogen group from *meta* to *ortho* to *para* positions in the ring results in a corresponding shift of the intensity center to the first or principal band. The shift of intensity in the alkali oxide series of cobalt glasses is another example of the same effect (Fig. 7.8). (See also Fig. 10.5-10.8 for similar effects in infrared spectra.)

CHROMOPHORES


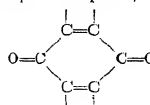


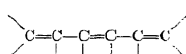
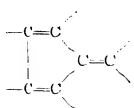
In the classification of colored or absorbing systems it is customary to ascribe to a certain part of the molecule the resonating effect which is considered as responsible for the color, and such a group is known as the *chromophore* (B21). The groups given in Table 7.2 are generally included in a list of organic chromophores.

TABLE 7.2
IMPORTANT ORGANIC CHROMOPHORES

(a) Simple

	Ethylene		Thiocarbonyl
	Azo		Azomethine
	Carbonyl		Sulfoxide
	Nitroso		

(b) Complex (involving two or more simple chromophores)

	Nitro		Quinone
	Azoxy		Ketene (cumulative unsaturation)
	Divinylethylene (conjugated unsaturation)		
	Fulvene		

Chromophoric changes may be resolved into two effects, intensity and frequency shifts, which are described as follows:

(a) **Hyperchrome:** An increase in the extinction value of the absorption band. *The intensity of the color increases.*

(b) **Hypochrome**: A decrease in the extinction value of the absorption band. *The intensity of the color decreases.*

(c) **Bathochrome**: A shift of the absorption band towards the red (lower frequency). *The color deepens* (i.e., a change from yellow, to red, to purple, to blue, to green).

(d) **Hypsochrome**: A shift of the absorption band towards the blue (higher frequency). *The color lightens* (i.e., a change from green, to blue, to purple, to red, to yellow).

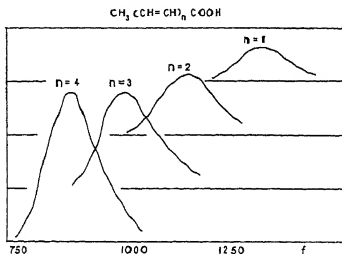


FIG. 7.10a.—Absorption spectra of unsaturated acids with conjugated ethenylene (—CH=CH—) linkages (Hausser [C64, C65]).

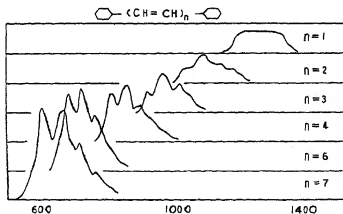


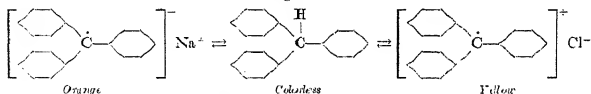
FIG. 7.10b.—Effect of conjugation in polyethenylene diphenyl derivatives (Kuhn [C74, C75]).

Many of the simple resonators or chromophores do not in themselves produce visible absorption. Ethylene, for example, has an absorption band at 1545 f (1950 Å) in the extreme ultraviolet, but the conjugated coupling of two or more ethylene radicals together results in both hyperchromic and bathochromic effects (Fig. 7.10). The actual effect seems

to be more nearly a multiplication of resonance than addition. The carotinoid colors, such as those found in the carrot and tomato, are typical of a long chain of seven to thirteen conjugated double bonds.

Wizinger (B56) has suggested the use of an ionic formula for the representation of a resonating system, and this, in many ways, is more satisfactory than the more rigid chromophore formula. For example, in the representation of triphenylmethyl it is difficult to explain the intensification of color on the change from neutral to acid or alkaline solutions, but in the ionic formula the representation is not difficult (Fig. 7.11).

Fig. 7.11

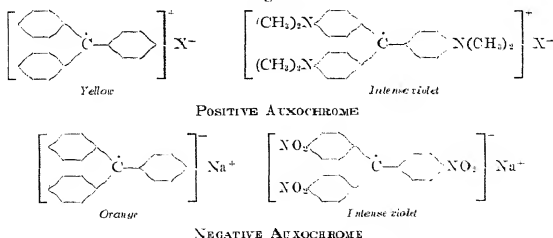


It would therefore appear that, in addition to the usual positive auxochromes, OH, OR, NH₂, NHR, NR₂, which cause color intensification and bathochromic effects (color deepening) in positive ions with a coordinated unsaturated central atom or resonating group, there are negative auxochromes, such as the NO, NO₂, CO, CN, SO₂, and N=N, which produce auxochromic and bathochromic effects in negative ions with a coordinated unsaturated central atom or resonating nucleus.

One might further extend this auxochrome-ion theory to include amphoteric auxochromes such as the C=C linkage which can act as an auxochrome or resonating amplifier in either positive or negative ions.

The examples of negative and positive auxochromes in Fig. 7.12 will serve to illustrate these effects.










Fig. 7.12



Whether one accepts the ionic, chromophore, or electron shift formulas for the production of color they are all merely graphical means of repre-

senting the same color effect. It should be remembered that the writing of a compound in a quinoid formula does not of necessity indicate that no benzene ring is present, but rather that it is capable of resonating between that and an ionic benzene structure. In the representation of the formulas of many dyestuffs and other absorbing groups we will use quinoid structures since they are the accepted form and are more easily visualized.

TABLE 7.3
WAVELENGTH AND FREQUENCY VALUES
FOR CHROMOPHORIC GROUPS

Group	λ	ν	ϵ
	280 $m\mu$	1076 f	
	186	1615	
	227	1325	
	366	820	
	302	994	
	180	1660	
	268	1120	39
	311	964	280
	476	800	9700

For some of the simple chromophores such as the carbonyl it is possible to assign a certain frequency of absorption (Fig. 7.13) as characteristic of this resonating group although it must be remembered that the attachment of radicals to the chromophore will result in a shift of frequency and intensity. The simple colored ions can also be assigned certain absorbing centers or bands as indicated in Table 7.3.

With ionizable substances or those which undergo a chemical reaction with the solvent there will be marked effects upon solution, dilution, or change of temperature (Fig. 7.14).

The effects of solvents may be divided into two classes: that in which a chemical combination takes place with the compound, and that in which the frequency of the absorption band is influenced by the polar

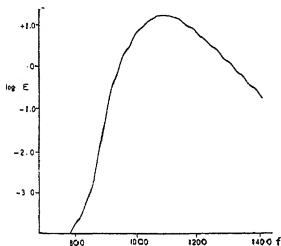


FIG. 7.13

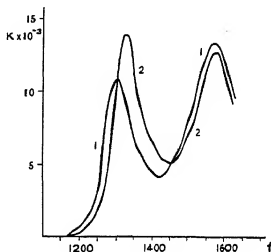
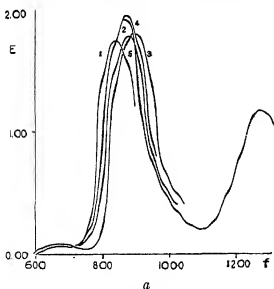


FIG. 7.14

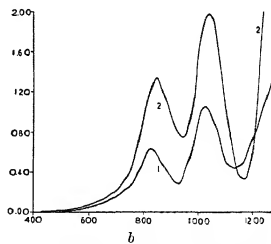
FIG. 7.13.—Absorption spectrum of acetone.

FIG. 7.14.—Temperature effect on absorption spectrum of the iodine ion in NaI—H₂O solution (Scheibe [1,20°; 2, 70°] [C103, B49]).

nature of the surrounding medium without any actual chemical combination with the solvent material (Fig. 7.15).



a



b

FIG. 7.15.—a. Effect of solvents on the absorption spectrum of benzeneazophenol. 1. Pyridine. 2. Methylalcohol. 3. Petrolatum. 4. Ethyl acetate. 5. Benzene. (Brode [C11].)

b. Absorption spectra of iodine in ethyl alcohol (1) and in KI solution (2). (Brode



It has been shown that in the simple C—C bond there is no apparent absorption in the visible or near ultraviolet as a result of the electronic resonance possibilities of the

C : C linkage. Infrared and Raman spectra are produced by simple compounds with such C—C linkages, but these spectra are characteristic of the simple linkage and not of the molecular resonance as a whole. The —C— linkage, since it does not transmit, to any extent, resonance vibration from one resonator to another, can act quite satisfactorily as an insulator between two chromophore groups. This is especially true of two methylene groups: —CH₂—CH₂—.

Inasmuch as the two isomeric forms of optical antipodes have the same energy content it would not be expected that they would have

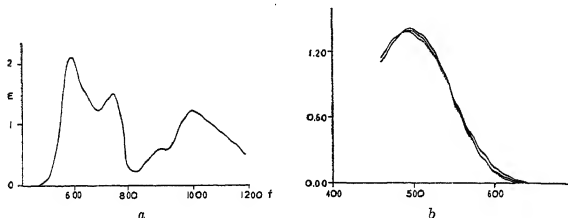
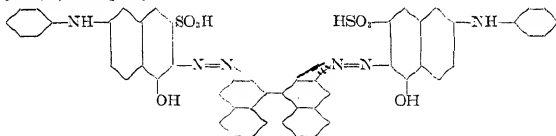


FIG. 7.16.—*a*. Absorption spectrum of *dl*-phenyl-(*p*-dimethylaminobenzenesulfonylamino)-acetic acid in alcohol. $C = 0.0125$ gram per liter; $d = 1$ cm. The absorption spectra curves of the *d* and *l* forms were also determined and found to be identical within the allowable experimental error. (Brode and Adams [C20].)

b. Absorption spectra of *d*-, *l*-, and *dl*-2,2'-bis(thylazo)-1,1'-binaphthyl.



(Involving molecular rather than atomic asymmetry.) Curves are identical within experimental error. (Brode and Brooks.)

different absorption, especially since they involve the same types of linkages, and this has been demonstrated by experiment (C20) (Fig. 7.16).

>C=C< Ethylene has an absorption band in the extreme ultraviolet (195 $m\mu$), and as a simple symmetrical unsaturated compound its absorption band is reasonably symmetrical (C36) (Fig. 7.17). Homologs of ethylene which are unsymmetrical show a distinct broadening of the band as would be expected.

—C≡C— Acetylene does not show any marked increase in absorption or any marked change in position of the absorption band (188–215 $m\mu$) as compared with ethylene, which confirms the chemical evidence that acetylene does not exhibit an appreciably greater activity or unsaturation than is shown by ethylene.

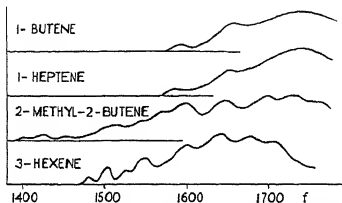


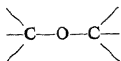
FIG. 7.17.—Absorption spectra of olefins (Carr [C'58]).

$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{—OH}$ The C—OH linkage exhibits only a slightly greater resonance than the C—C linkage, and, as might be expected, the simple alcohols in a pure condition are transparent up to the limit of the normal photographic plate (200 $m\mu$). They are therefore quite suitable as solvents for spectrophotometry within this region.

NOTE. Although alcohols are indicated as possessing little absorption, due care should be taken in the use of alcohol as a solvent to insure purity. Absolute ethyl alcohol often contains benzene which makes it unfit as a solvent for ultraviolet absorption spectrophotometry.

$\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{—X}$ Ethyl iodide shows a single band at 250 $m\mu$ which is not appreciably changed by alteration of the solvent from carbon tetrachloride to hexane to ethyl alcohol although its extinction is reduced by the use of water as a solvent. Iodoform (CHI_3) shows absorption bands at 348, 307, and 275 $m\mu$, and a fourth is indicated in the extreme ultraviolet. In the cases of the simple C—Cl and C—Br linkage there is very little absorption within the spectrum down to 200 $m\mu$.

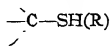
X—C=C—X The combination of halogens and ethylene resonating systems presents an interesting study on account of the different energy values of the cis and trans forms. The cis forms, as might be expected from their lower stability, have slightly greater absorbing properties than the trans forms (Fig. 7.18).



Ethers possess the property of coordination and, as such, might be expected to show some absorption, but in their noncoordinated form, especially if the —O— linkage is buried well within the molecule, it has much the same resonating property as a —CH₂— linkage. This property of the oxygen

linkage to act as a non-transmitter of resonance or a shock-absorber is well demonstrated in the failure of the change of the R group in R—O—C₆H₅—N=N—C₆H₅OH to alter appreciably the nature of the absorption spectra of the resonating chromophore.

Similar studies on the change of color of thiophenolic compounds indicate that sulfur is also a resonating insulator.



C=O The ultraviolet absorption spectrum of acetone

(Fig. 7.19) shows a strong absorption band at 1110 f (270.6 mμ) in an alcohol solution. The increase in

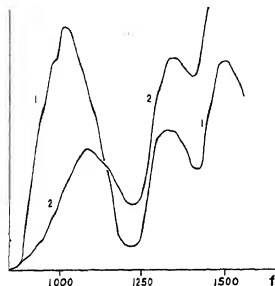


FIG. 7.18.—Absorption spectra of trans (1) and cis (2) stilbene in ethyl alcohol (Smakula and Wassermann [C107]).

size of the alkyl radicals in the ketone produces a slight increase in the extinction coefficient and a slight reduction in the frequency of the absorption band. Acetaldehyde shows absorption at about the same frequency as the acetone band, but at a somewhat lower extinction coefficient. In a nonpolarizing solvent, such as hexane, the carbonyl band shows an increase in extinction.

In addition to this hyperchromic and hypsochromic effect due to a change in hydrocarbon content of the alkyl radicals attached to the carbonyl, an even greater effect is produced on the carbonyl absorption band as a result of a tautomeric equilibrium between enol and keto forms (a), and in the complete elimination of the unsaturated condition in the molecule through hydration or a similar reaction (b).

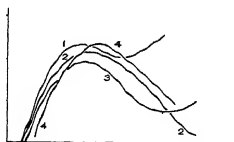
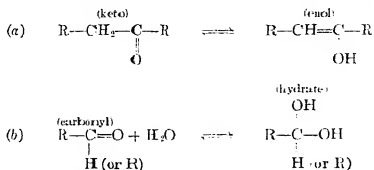


FIG. 7.19.—Absorption spectra of propylethyl ketone (1), acetone in alcohol (2), acetaldehyde (3), and acetone in hexane (4).

The tautomeric equilibrium effect (a) is easily demonstrated in the 1,3-diketo compounds, such as acetoacetic ester and acetylacetone (see the discussion in this chapter on conjugated chromophores). The reduc-



tion, by the addition of alkali, of the extinction coefficient of the absorption band produced by acetone and other carbonyl compounds is

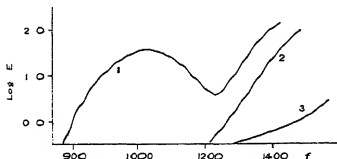


FIG. 7.20.—Absorption spectra of (1) chloral in hexane; (2) chloral hydrate in water; (3) formaldehyde in water (Schou [C'8]).

explained on the formation of a salt with the hydroxyl hydrogen of the enol form.

With regard to the hydration effect (b) the difference between the absorption spectra of chloral, $\text{CCl}_3-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{O}$, and chloral hydrate,



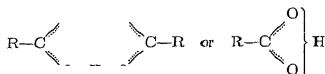
$\text{CCl}_3-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{OH}$, and the failure of formaldehyde, which shows a marked

absorption in the vapor state (Fig. 7.1) and in hexane solution, to show appreciable absorption in an aqueous solution (Fig. 7.20) are sufficient to demonstrate this structural change.

>C=S The increased mass and resonating property of the sulfur atom as compared with the oxygen atom will naturally give rise to a bathochromic and hyperchromic effect with an increase in absorption and a shift of the band to lower frequency. The change from

oxygen to sulfur in colorless benzophenone yields a blue thiobenzophenone.

$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \\ \diagup \\ \text{OH} \end{array}$
 Acids, in a similar manner to formaldehyde, undergo, in water, association and hydrolysis with a loss of their carbonyl structure:



The hydroxyl group apparently inhibits the resonance or existence of the carbonyl group, and most of the simple aliphatic acids are transparent down to 220 or 230 $m\mu$. The presence of a carboxyl group in a molecule does, however, affect the resonance of other groups in the molecule even though it is not conjugated or in juxtaposition to the other resonating group. This is nicely demonstrated by the unsaturated fatty acids (Fig. 7.21), in which there are one, two, or three ethenylene

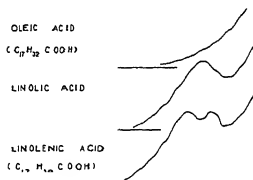


FIG. 7.21.—Absorption spectra of non-conjugated unsaturated fatty acids. An increase in the number of ethenylene linkages increases the number of bands without a bathochromic or hypsochromic effect. Oleic acid has one double bond ($\text{C}=\text{C}$), linoleic has two, and linolenic has three. (Brode and Tryon [37].)

groups, none of which are conjugated with each other or with the carboxyl group. Since in the chain of atoms some groups must be farther from the carboxyl group than others, we would expect, and do find, that with an increasing number of unsaturated linkages an increasing number of band maxima appear at slightly different frequency values.

— COOR Esters like their parent components, alcohols and acids, show only slight absorption, and that in the extreme ultraviolet.

— CONH_2 The combination of other groups such as NH_2 to the carboxyl to form an amide fails to alter appreciably the absorption spectra of the compound.



As might be predicted from the similar properties of water and ammonia, amines will tend to show more absorption than alcohols. The slight increase in resonance is sufficient, however, to bring the absorption band just within the photographic range. The absorption of amines is reduced as one goes from the pure compound to solutions of hexane, alcohol, water, and, lastly, acids (salt formation) in which the solution is completely transparent within the photographic range.

NH₂-ACIDS Combinations of acids with amines within the same molecule, such as the alpha-amino acids, usually result in inner salts, and hence we may expect protein material to show little absorption except for aromatic or other resonating groups which are present. The same may be said with regard to the hydroxy acids (**OH-ACIDS**). Polyhydroxy aldehydes (**OH-ALDEHYDES**), which are the principal constituent groups of the carbohydrates, will show absorption only when a free carbonyl group or unsaturated linkage is present.

-NO₂, -NO₃ The nitro, nitrite, nitroso, nitrosamine, and nitrate derivatives of organic compounds all show absorption which is due to the **-N=O** group, a powerful resonator producing bands in the near ultraviolet and visible region of the spectrum. Nitrobenzene has a very intense band at 294 mμ which starts in the visible as evidenced by its natural yellow color. Nitro and nitroso compounds, especially the latter, are extremely powerful chromogens, e.g., nitroso tertiary butane, (CH₃)₃C-NO, is a brilliant blue compound, and nitrosobenzene, C₆H₅-NO, a green compound.

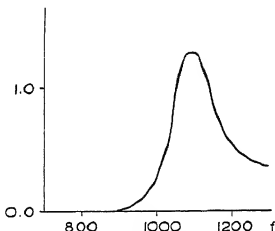
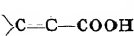
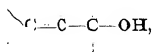


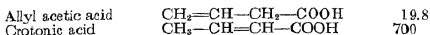
FIG. 7.22.—Absorption spectrum of Osajin.

CONJUGATED AND ADJACENT CHROMOPHORES



Allyl alcohol, CH₂=CH-CH₂OH, shows a weak band in the photographic region at 234 mμ and a strong band at 193 mμ, indicating a slight conjugation. This is in line with the increased chemical activity of both the C=C and OH resonators. Crotonic acid, CH₃-CH=CH-COOH, with a carboxyl group conjugated with the ethylene group, also shows a marked increase in extinction and a slight shift of the unsaturated ethylenic absorption

bond towards higher wavelength (lower frequency) values. As one moves the double bond out of conjugation with the COOH there is a marked drop in the extinction, and the compound reverts to what might be considered a simple mixture of the component resonators:



The combination of an ethenylene and carbonyl group, as might be predicted from the strong absorption of the separate groups, results in

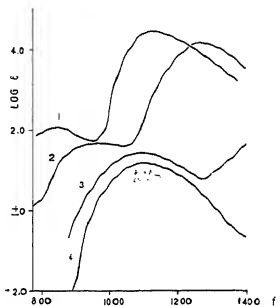


FIG. 7.23.—Absorption spectra of (1) phorone, $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(=\text{O})-\text{CH}=\text{C}(\text{CH}_3)_2$; (2) mesityloxide, $\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{C}(=\text{O})-\text{CH}_3$; (3) allylacetone, $\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)-\text{CO}-\text{CH}_3$; (4) acetone, $\text{CH}_3-\text{CO}-\text{CH}_3$. (Ley-Henri-Scheibe [B. 20].)

marked intensification of absorption and a bathochromic effect in the shift of the absorption band to a lower frequency (Fig. 7.23).

$\text{>C}=\text{C}=\text{O}$ The shared rather than conjugated combination of ethylene and a carbonyl group yields a resonating system which, in part, is dampened by the close proximity of the resonating parts, and in part is converted into a new triatomic resonator yielding different bands from the original component groups. Ketene, $\text{CH}_2=\text{C}=\text{O}$, exhibits two bands at $324.4 \text{ m}\mu$ and at $267.1 \text{ m}\mu$, and a third, indicated at about $230 \text{ m}\mu$. Diethyl ketene shows absorption bands at 373.5 and $224.1 \text{ m}\mu$. In both cases the band in the neighborhood of $230 \text{ m}\mu$ is very intense as compared with the band at the shorter-wavelength position. In the vapor state ketene shows a fine structure system, such as

formaldehyde shows, and at about the same position as the solution bands of the compound. There is little doubt but that the close coupling of the two resonating groups in ketene has resulted in the formation of a new coupled chromophore or resonating system.

$\text{C}=\text{C}-\text{C}=\text{O}$ The combination of an ethylene and carbonyl resonator in a conjugated coupling (alternate double- and single-bond arrangement) results in hyperchromic and bathochromic effects (intensification and shift to lower frequency values) which are almost equivalent to a new resonating system involving the two units together as the single resonator (Fig. 7.23). Some of our best examples of such compounds are to be found in the derivatives of acetoacetic ester (*a*) and the 1,3-diketones (*b*) in their enol forms.

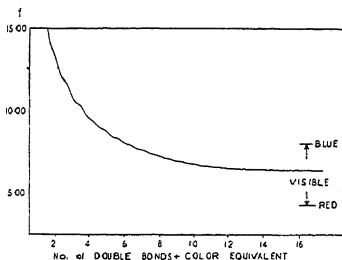
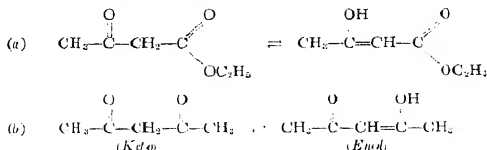


FIG. 7.24.—Shift of absorption band with increase in number of double bonds in $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_n-\text{C}_6\text{H}_5$ (Hausser). See Fig. 7.10 for examples of the absorption spectra of compounds indicated (C64).



In the equilibrium between the enol and keto forms the enol form possesses a $\text{C}=\text{C}-\text{C}=\text{O}$ structure which provides a means of determining the amount of enol form in this equilibrium through the absorption spectrum of the solution. A comparison of the absorption spectra of a series of such compounds will illustrate the application of this method and the effect of certain solvents in inducing or repressing the equilibrium toward the enol form.

>C=C-C=C< Conjugated ethenylene linkages, like the conjugated ethenylene-carbonyl grouping, result in interresonance, the shift of the band toward the visible from the ultraviolet, and marked increase in intensity. Hauser has examined the unsaturated acid and diphenyl derivatives with conjugated double bonds, and his series of curves give a very good illustration of the effect (Fig. 7.24). As the number of conjugated linkages are increased, the rate of shift of the frequency and intensity of the band decreases so that the possible shift of the band is subject to a limiting condition. This limit of shift,

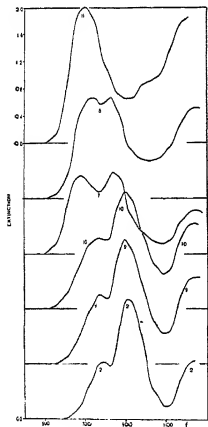
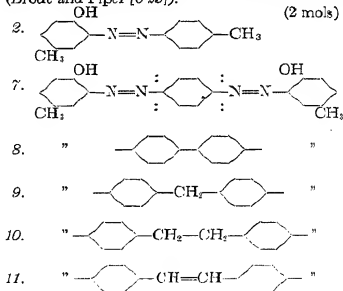


Fig. 7.25.—Absorption spectra of chromophores linked by conjugated and non-conjugated groups (Brode and Piper [C 29]).



together with the decrease of stability, is one of the important factors which prevents the easy extension of the range of sensitization of photographic plates for the infrared. Brooker and Hamer have shown (Fig. 9.22) (C34, C49) that as one increases the number of conjugated ethenylene linkages between two resonating groups in the cyanine type of dye there is a shift of sensitization property toward lower frequency which is concomitant with the shift in absorption center and decrease in stability of the dye. Modifications which may be incorporated into the dye structure and which may improve the stability include such effects as weighting of the long conjugated chain at some point between the two end resonators. In general the introduction of ethenylene groups between

two resonators is of an auxochromic character in that the band is given a bathochromic shift and an increase in intensity (Fig. 7.25).

Quinones The *ortho* and *para* quinones are special cases of the combination of several resonating carbonyl and ethenylene groups. In view of the large number of possible resonating systems which may be postulated in these compounds and the fact that some are conjugated and some are adjacent, it becomes extremely difficult to assign to any one particular group the specific absorption effect observed in a given portion of the spectrum. It is more apparent that the combination

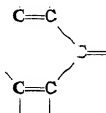
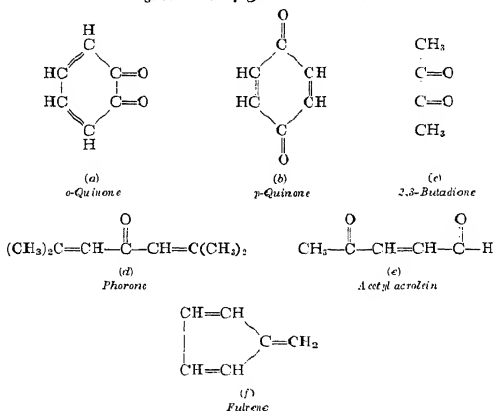


Fig. 7.26 Conjugated Resonators

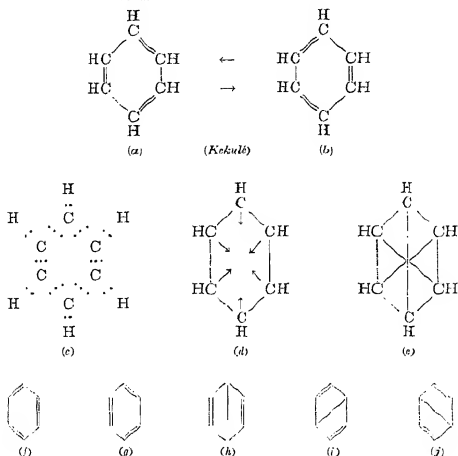


or grouping of resonators can be considered a unit system of resonance or vibration. It is possible to make some comparison between such structures as 2,3-butadiene (c) and *o*-quinone (a). Similar comparisons can be made between phorone (d), *p*-quinone (b), acetyl acrolein (e) and fulvene (f), (Fig. 7.26). With the increase in resonance properties of a molecule there is a corresponding shift toward the visible from the ultraviolet, and an increase in intensity, together with a resolution effect. The band becomes resolvable, in many cases, into structural components which have an approximate constant frequency separation, and the ob-

served frequency of the absorption band component is an integral multiple of this constant frequency difference. This apparent simplification of the absorption band structure as one increases the resonance complexity of the molecule lends support to the theory that the more complicated molecular absorbing units may act as a single resonator and, because of their size, respond more like a simple harmonic vibrating system.

Fig. 7.27

Structural Formulas of Benzene



Resonating Forms (Pauling)

Benzene and Aromatic Compounds. The conjugation of ethenylene linkages results in a decrease in chemical activity and an increase in stability of the unsaturated linkages in the middle of the conjugated chain, and an increased activity of the end groups in the conjugated chain. Benzene, because of its unusual structure, may be considered as an endless conjugated chain, in that the bonds continue in conjugation as one goes around the ring. One may further postulate a resonating system for benzene as oscillation between the two Kekulé formulas (Fig. 7.27 a and b). Many other formulas have been proposed for benzene, such as the three electron sharing formula (c), the Arm-

strong-Baeyer formula (*d*), and the Claus formula (*e*). Whatever formula is accepted, however, it must permit of marked stability and resonance. Pauling (*B44*) has indicated that the resonating formulas can best be explained by the forms *f g h i j*, in which the major resonating system is represented by *f* and *g*. Benzene is in itself a very symmetrical molecule, and as such we would expect it to have a very symmetrical and well-defined absorption spectrum. In the vapor state, benzene exhibits a band spectrum (Fig. 7.28) with a remarkable resolution of the band components. As can be seen from Table 7.4, the bands appear to be multiples of a band which is known to exist in the infrared at a frequency value of 30.2 f.



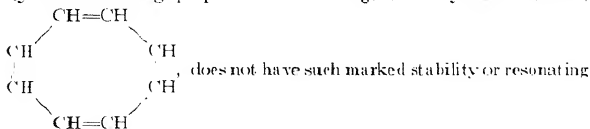
FIG. 7.28.—Absorption spectrum of benzene (vapor). P.

TABLE 7.4

ANALYSIS OF THE BENZENE ABSORPTION BAND (Fig. 7.2b)

Component	Multiple	Fundamental Frequency	Calculated	Observed
A	37	× 30.2 f	= 1117 f	1118 f
B	38	× 30.2	= 1148	1149
C	39	× 30.2	= 1178	1178
D	40	× 30.2	= 1208	1209
E	41	× 30.2	= 1238	1235
F	42	× 30.2	= 1268	1268

The freedom from ring strain in the benzene nucleus as well as its planar structure must have a great deal to do with the marked stability and resonating properties of the ring, since cyclooctatetraene,



power. Internal or external forces tend to inhibit the resonance of the molecule, as is evidenced by the influence in solution of solvents, especially polar solvents, on the benzene absorption spectrum. Internal forces may be described as actual molecular combination with the ben-

zene ring, such as the substitution of methyl, carboxyl, hydroxyl, and similar groups (Fig. 7.29) in which there is practically always, a resonance dampening. The fine structure of the benzene absorption is often

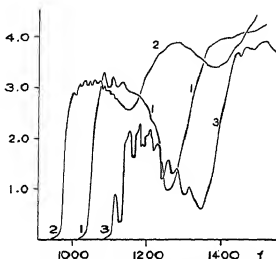


FIG. 7.29.—Absorption spectra of benzene and substituted derivatives: 1, phenol; 2, aniline; 3, benzene. (Klingstedt-Brode [B20].)

obliterated by this dampening effect, although the added group may be an auxochrome in character and may markedly increase the absorption as well as shift the band towards the visible.

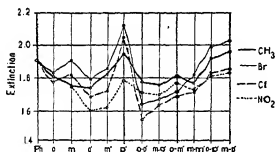


FIG. 7.30a.—Influence of position of substitution in benzenazophenol on the extinction coefficient of the absorption band (Brode [C9]).

The influence of position of substitution by weighting groups is demonstrated by the studies of the author (C18) on the azo dyes. Figs. 7.30a and 7.30b show that as the position of substitution is varied in either benzene or naphthalene there is a definite effect on the absorption band frequency and extinction. In particular it is to be noted that certain substitutions placed *ortho* to the chromophore create a marked inhibition of the extinction values

while substitutions *para* to the chromophore or *ortho* to a *para* substituted auxochrome create an enhancement of these properties. In certain solvents there appears to be an equilibrium between two forms with slightly different frequency of absorption bands, and this equilibrium is markedly influenced by the position of the substituting group.

As might be expected, the naphthalene and higher aromatic hydrocarbons, which may be considered as resonator substituted benzene

compounds, show a shift and intensification of the absorption band but without much loss in the band structure resolution in the vapor and

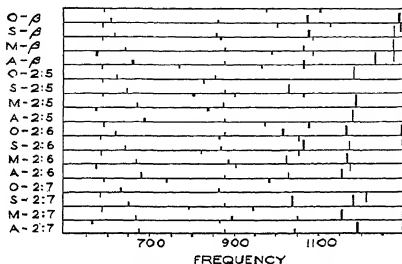


Fig. 7.30b.—Frequencies of the principal maxima of monazo dyes prepared by diazotization of aniline (*A*), sulfanilic acid (*S*), metanilic acid (*M*), and orthanilic acid (*O*), and coupling the diazonium salt to beta-naphthol (β) and the corresponding 5-, 6-, and 7-sulfonated derivatives of β -naphthol. The length of the lines indicates relative intensity of the absorption band. Lines pointing upward represent maxima observed in a neutral (water) solvent; lines pointing downward represent maxima observed in an acid (HCl) solvent. (Brode, Griffith, and Eberhart [C23; C25].)

solution states (C42) (Figs. 7.31 and 7.32). It is difficult to say which group is to be considered the chromophore and which the auxochrome,

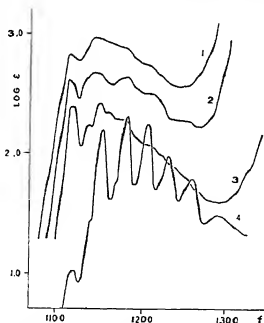


Fig. 7.31.—Absorption spectra of polyphenyl compounds: 1, triphenylmethane; 2, diphenylmethane; 3, toluene; 4, benzene (Ley-Orndorff [C77]).

when the benzene ring and another resonating group are attached in alternate position. The marked stability of the benzene resonator and

the known fact that chromophoric groups in the center of a chain of conjugated resonators are stabilized by the end resonators makes it

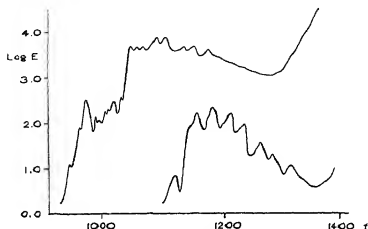
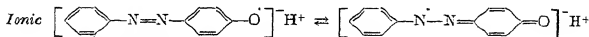
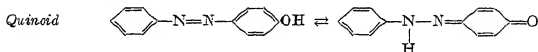


FIG. 7.32.—Absorption spectra of naphthalene (upper) and benzene (lower) (de Lasslo-Henri [C42]).

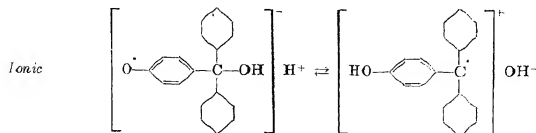
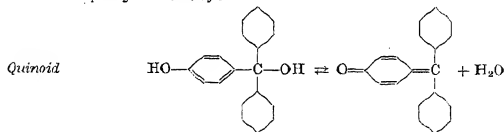
possible to prepare fairly stable resonating compounds with benzene rings at each end and resonators in the middle. Similar compounds with

Fig. 7.33 Quinoid and Ionic Resonating Structures

A. Azo dye



B. Triphenylmethane dye



aliphatic end groups would normally be unstable. Examples of such aromatic compounds include the azo dyes and triphenylmethane free radicals (Fig. 7.33).

The combination of two or more aromatic rings may take the form of the polycyclic compounds such as naphthalene and anthracene which have been discussed and whose resonance forms have been rather carefully studied (B44). A second type of coupling is that of the diphenyl series in which the molecule still acts as a single resonator since the benzene rings are conjugated together. A third type is that in which the rings are separated by a single carbon linkage, in which case we may expect more or less simple addition of the resonating effects of the separated chromophores (Fig. 7.34), except in so far as the single carbon may be able to transmit resonance effects. This transmission of resonance effects by a single carbon is very slight as can be seen in

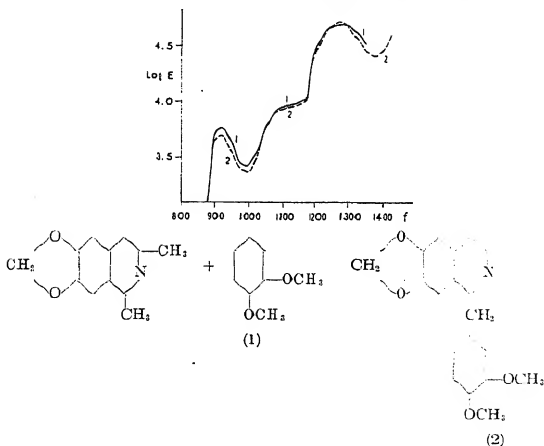


FIG. 7.34.—Insulating effect of methylene ($-\text{CH}_2-$) linkage between chromophores. Absorption spectra of: (1) veratrol + 1,3-dimethyl-6, 7-methylenedioxyisoquinoline; (2) homoveratryl-3-methyl-6, 7-methylenedioxyisoquinoline. (Gerendas, Varga, and Fordor [C51].)

such examples as that of the azo dye series (Fig. 7.25). The separation of resonating groups by two methylene ($-\text{CH}_2-$) groups is even more effective in preventing resonance transfer, but the change of the $-\text{CH}_2-\text{CH}_2-$ to a $-\text{CH}=\text{CH}-$ group results in the direct coupling together of the resonating groups, and an increase in the number of these $-\text{CH}=\text{CH}-$ groups between the end resonating systems results

in a marked increase in the absorption as well as a shift to lower frequency values.

It is thus apparent that the ethenylene linkage produces a single resonator from the two resonating groups by means of its transmitting properties, and at the same time through its chromophoric and auxochromic properties produces a still larger and more powerful resonator.

While it is expected that the simple compounds di- or triphenylmethane will not have conjugated benzene rings, the formation of a chromophore with the methane carbon such as is produced in the di- and triphenylmethane dyes results in two resonating systems, both conjugated to the chromophore. A simpler case of crossed conjugation is found in the fulvene structure with a marked increase in absorption. As was explained in the earlier discussion on resonance and valence it is not necessary to consider that a quinone structure actually forms, but rather that the carbon of the methane portion may be considered as a charged and resonating unit, with which the benzene rings are conjugated.

SUMMARY OF ABSORPTION SPECTRA EFFECTS

The absorption of light by organic and inorganic molecules is due to a resonator or group of resonators. These resonators may be coupled or separated in the molecule, and if coupled they may be directly coupled, known as cumulation, or coupled through a single bond, conjugation. For the most part, resonating atoms or groups of atoms contain unsaturation or an incomplete inner shell of electrons. To each of these resonat-

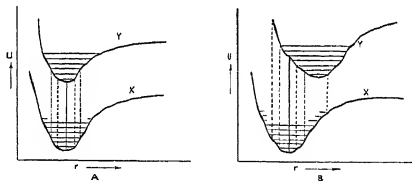


FIG. 7.35.—Franck-Condon electron vibration curves of symmetrical (A) and unsymmetrical (B) shifts.

ing groups may be assigned a certain frequency factor, but it is difficult to predict from these values (Tables 7.3 and 10.1) the absorption bands of a complex molecule unless each resonator is independent and well shielded from the other resonating systems. The close proximity or conjugation of resonators results in bathochromic and hyperchromic effects which are not easily predictable. In addition to these resonators or chromophores there are a number of groups which are known as auxo-

chromes or amplifying groups, which in themselves do not always produce resonance but have a powerful effect on the resonance of other systems. These auxochromes may be classed as positive or negative, and their effect varies with the position of attachment of the group to the resonating system.

For complicated resonating structures there seems to be little hope at the present time of complete analysis of the resonating system. The absorption spectrum does, however, act as a fingerprint or identification for very complicated structures, including the quantitative estimation as well as qualitative identification of the substance. The standard method for the determination of the amount of vitamin A in cod-liver oils and extracts is by the extinction coefficient of its absorption spectrum band at $328\text{ m}\mu$ (Morton, *B41*). On account of the large number of resonating systems, the possible combinations of these resonators, and the rather broad and diffuse nature of most absorption bands, it becomes almost impossible to classify absorption band systems in accordance with the resonator in anything like the exact order used in the classification of emission spectral lines of elements.

POTENTIAL ENERGY CURVES

Although it is outside the scope of the present book to discuss the field of photochemistry it would be well to call attention to the principles of Franck and Condon concerning the energy-frequency shifts in electron

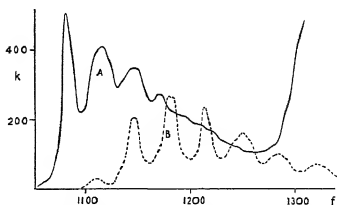


FIG. 7.36.—Absorption spectra of *p*-chlorotoluene (*A*) and benzene (*B*). Illustrates symmetrical shifts (*A*) (intensity concentrated in 0,0 band) and unsymmetrical shifts (*B*) (intensity concentrated in bands other than 0,0). (Sheibe and Fromel [*B49*].)

emission and absorption. (*A20*) Fig. 7.35*A* gives the energy pattern for a symmetrical, and *B*, for an unsymmetrical, shift. Such curves as those in Fig. 7.36 would be typical of such energy patterns. The symbol r represents the distance between the vibrating atoms, and U the potential energy. As would be expected, the energy required to push the atoms together increases very rapidly, while the energy required to pull them

apart increases to a certain point and then approaches a constant, which is the measure of the energy required to dissociate the atom from the molecule and the limit of the band system. The change from one electronic state to another (represented by Y and X in each figure) by absorption or emission will result in a symmetrical series of frequency values (concentration of intensity in the (0,0) first bands), if the two energy curves are of symmetrical shape and centered. If there is an unsymmetrical condition, as in (B), we may expect an unsymmetrical absorption curve such as Fig. 7.36B in place of the symmetrical curve (i.e., maximum of intensity at bands other than the (0,0) band).

Such effects as predissociation, continuous emission, and continuous absorption spectra can be indicated by special cases of these potential energy—nuclear separation ($U-r$) curves.

LITERATURE

General

"Optical Basis of the Theory of Valence." R. de L. Kronig (A44).

"Beziehungen zwischen Absorption und chemischer Konstitution." H. Ley (B33).

"Molekulspektren von Lösungen und Flüssigkeiten." G. Scheibe and W. Fromel (B49).

Reference

Watson (B54), Martinet (B38), Heinrich (B21), Cohen (B7), Ramart-Lucas (B48), Brode and Leermakers (B5), Glasstone (A20), Wizinger (B56).

CHAPTER VIII

ABSORPTION SPECTRA (APPARATUS AND METHODS)

SPECTROPHOTOMETERS

The earliest data on absorption spectra reported the absorption band edges in the observed spectrum (Fig. 8.1). The ease with which it was possible to dilute the solution or change the cell thickness led to the observation that as a solution was diluted its absorption band was nar-

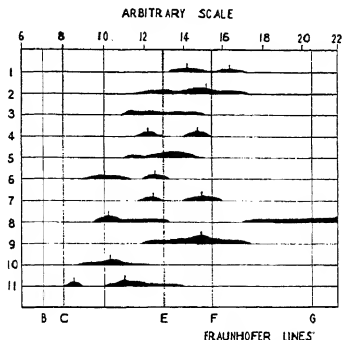


FIG. 8.1.—Qualitative indication of absorption spectra (after Formanek [B12] and Watson [B54]).

1. Orange II. 2. Fast red A. 3. Fast acid fuchsin. 4. Chromotrope 2R. 5. Azo fuchsin B. 6. Victoria violet. 7. Ponceau 4RB. 8. Diamond green. 9. Congo red. 10. Diamine blue 3B. 11. Azo blue.

rowed and reduced in intensity. The plotting of the observed cut-off or extinction values against the concentration or thickness produced the absorption curve for the observed material. The values thus obtained were a fairly good approximation to our more accurate absorption measurements of today, but were individually characteristic for each observer, since the density or extinction point at which the observer was to decide that the band terminated was of a nebulous character. Fig. 8.3 shows examples of this type of data as compared with the same curve (Fig. 8.2.

Table 8.1) which has been accurately determined by a spectrophotometric method.

TABLE 8.1

<i>E</i>	No. obs.	Av. val., <i>f</i>	Av. dev.	Max. dev.	No. obs.	Av. val., <i>f</i>	Av. dev.	Max. dev.	No. obs.	Av. val., <i>f</i>	Av. dev.	Max. dev.
0.00	6	<580								
.05	4	630	10.0	10.0	4	720	20	30	4	824	2.0	6.0
.10	6	835	1.5	5.0
.15	1	838
.20	5	840	0.4	1.0
.25	1	843
.30	10	845	1.5	3.0	10	1138.4	7.0	18.0	8	1187	11.0	28.0
.35	1	848	1	1123	1	1210
.40	6	849	1.0	2.0	6	1107.5	4.0	8.0	6	1235	4.0	7.0
.45	1	852	1	1110	1	1242
.50	5	855	1.0	2.0	5	1088	5.0	9.0	5	1250	2.0	6.0
.55	2	856.5	0.5	0.5	2	1083.5	0.5	0.5	2	1256.5	1.5	1.5
.60	11	859.4	1.0	4.5	11	1075.5	4.0	6.5	9	1259.5	2.5	5.5
.65	1	860	1	1071	1	1264
.70	6	865.3	2.0	3.7	6	1061	3.0	4.0	6	1266	3.0	4.0
.75	1	870	1	1054	1	1270
.80	6	875.3	1.0	2.7	6	1046	3.0	6.0	6	1273	3.0	3.0
.85	1	877	1	1043	1	1285
.90	6	880.6	1.0	2.4	6	1035.5	2.5	3.5	5	1287	5.0	11.0
.95	1	881	1	1036	0
1.00	11	885.3	1.0	2.7	11	1026	3.5	7.0	7	1306	7.0	16.0
1.10	4	889.8	0.2	0.8	4	1013	3.0	5.0	1	1325
1.20	4	898.5	0.8	1.5	4	1000.5	3.0	7.5	1	>1380
1.30	4	900	0.2	1.0	4	990	4.0	6.0
1.40	7	908	4.0	9.0	7	981	4.0	7.0
1.50	12	927	7.0	17.0	12	965	8.0	15.0

Concentration, 3.3 g. dissolved in 100 cc. of 95% alcohol; cell thickness, 0.5 cm.

From the work of Lambert and Beer we know the relationship between absorption and thickness, and between absorption and concentration. These relationships may be expressed as

where E = extinction or the logarithm of the ratio of the incident to the transmitted light. Lambert's law more specifically indicates that the extinction, E , is a linear function of d , the thickness of the solution or solid, and Beer's law that the extinction is a linear function of the concentration, c , of the material. It therefore follows that the intensity, I , which is transmitted by the solution will vary inversely as the logarithm of the concentration or thickness, so that the logarithm of the thickness or concentration will appear as a linear function of the extinction. A number of collected tabulations or figures have been made of organic and inorganic compounds, based on the variation of thickness or concentration, or the introduction of a neutral gradient wedge (*B39*, *B19*) (Fig.

8.4). See also Fig. 12.46 for apparatus. In some cases a rough visual curve was drawn by the observer from his opinion as to relative brightness of

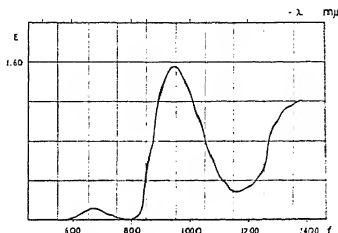


FIG. 8.2.—The absorption spectrum of azobenzene.

the spectrum or density of absorption. In other cases a more exact determination was made by a series of dilutions and an attempt to match

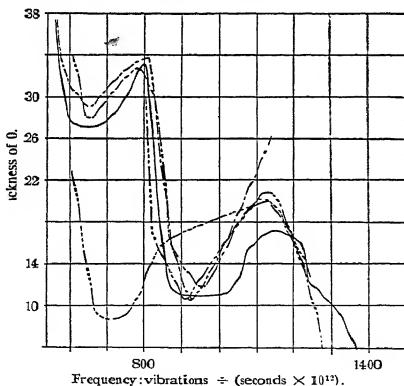


FIG. 8.3.—The absorption spectra of azobenzene in alcohol as determined by Baly and Tuck (solid line); Baly and Hampson (one dot); Hantzsch (two dots); Purvis and McClelland (three dots), and in concentrated hydrochloric acid by Tuck (four dots).

them at a given density. The Baly tube, a cell of adjustable length, was found to be very useful in the preparation of this type of absorption data (Fig. 8.5).

The next improvement in instrumental construction was the optical projection on the slit of the spectroscope or spectrograph of two images, that of the original beam and that of the beam after passage through the solution under investigation. Among the various methods are the use of a biprism (*a*), Albrecht rhomb (*c*) (sometimes called a Hufner Rhomb), Brace prism, Lohmeyer-Brodhun cube (*b*), two right-angle prisms



FIG. 8.4.—Wedge spectrogram of Rose Bengal 5B 1/4,000 (Mees [539]).

(d_1 and d_2), and polarizing prisms (*A15*) (Fig. 8.6). By means of such devices it was possible to compare the total absorption of the solution, or, with a cell in both beams, to compare the spectral absorption intensities of two separate solutions. In the comparison of the absorbing solution against the original light source it is obvious that the intensity of the unabsorbed beam will always be as great as or greater than the intensity

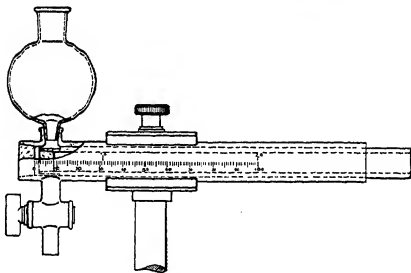


FIG. 8.5.—Baly tube for variation of cell thickness (Zeiss).

of light from the partially absorbed beam. The next improvement was a means of reducing the intensity of the comparison beam, by the introduction of some absorbing material into this beam. This absorbing material must have a uniform absorption for all wavelength values and should, if possible, be adjustable in density over a series of different values which in turn could be standardized in terms of absolute transmission. The use of a double-jaw slit as a mechanical means of light reduction

PHOTOMETERS

has been tried with reasonable success (*C118*). The combination of spectroscope and diaphragm-slit in one piece was not found to be very practical, so the mechanical slit or diaphragm devices were separated from the spectroscope slit. Mechanically operated devices on present-day ma-

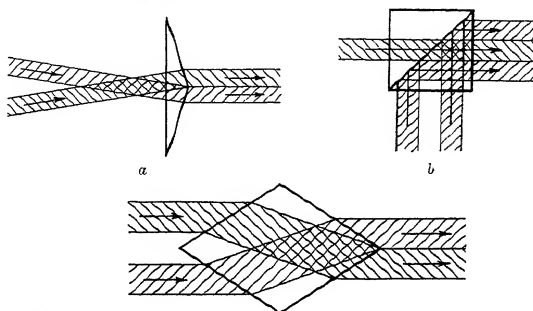


FIG. 8.6.—Optical devices to bring two light beams into juxtaposition.

chines include the rotating sector, the Judd Lewis vane photometer, the Spekker diaphragm photometer, wire or ruled quartz screens of known transmission value, and partly silvered or aluminized filters. Among the most satisfactory types of photometer devices for matching the two

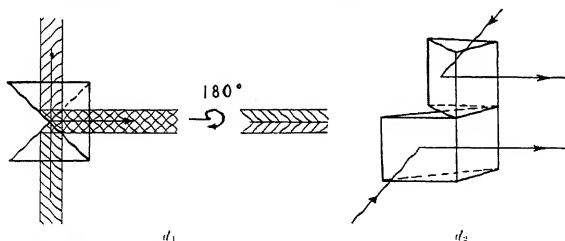


FIG. 8.6 (cont.).—Optical devices to bring two light beams into juxtaposition.

beams are those using the polarizing principle. In such instruments the two beams from the solvent and solute are polarized in opposite directions and brought in parallel through a second (analyzer) polarizing prism. This analyzer prism upon rotation alternately extinguishes and

transmits the two beams with a match of the two beams somewhere between each of these extinction angles. The Hilger-Nutting, Bausch and Lomb visual instrument, Jobin and Yvon, König-Martens, and Hardy

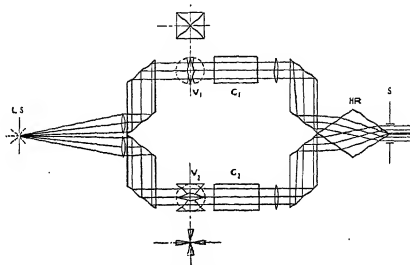


FIG. 8.7.—Judd-Lewis photometer (mechanical-vane type). v = vanes; c = cells; HR = Hufner Rhomb. (B30)

spectrophotometers all apply this photometer principle. Diagrams and photographs of certain of these instruments which represent the types

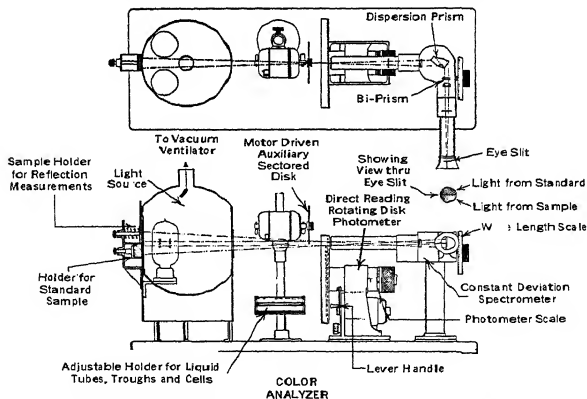


FIG. 8.8.—Rotating sector spectrophotometer (Keuffel and Esser).

indicated above are given in Figs. 8.7, 8.8, and 8.9 (see also Fig. 8.27 and 12.28).

The Keuffel and Esser instrument is of interest in that it uses a high-speed sector for visual determination, depending on the inability of the eye to distinguish a rapid flicker of high intensity from a continuous weaker intensity. This high-speed sector is adjustable while running so that the instrument becomes as simple to operate as the rotating prism types. The Hilger sector photometer, the Bausch and Lomb ultraviolet photometers, the Zeiss photometer, the Gaertner photometer, and many others employing photographic methods of recording are constructed with rotating sectors as a means of reducing the intensity of one beam as

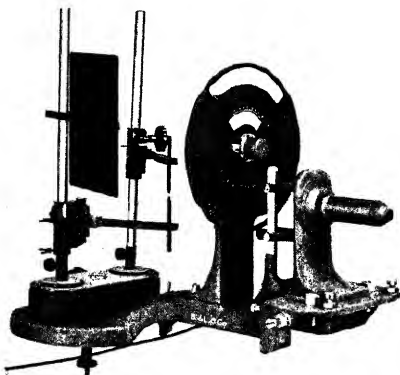


FIG. 8.9.—Ultraviolet sector photometer (Bausch and Lomb).

compared with the other, and the final image on the photographic plate is produced by a series of intermittent exposures of variable length. On the assumptions that the photographic process (see section on photography, Chapter XIII) does not involve an inertia at the start of exposure, or continuation of action after exposure, and that the density of the image is a linear function of the product of the intensity of light and the exposure time, the substitution of sectors for diffusing screens, wedges, or polarizing devices is quite acceptable. For a time it was thought that the sector method had quite an appreciable error due to variation in these factors, but it has been shown (*CS6*, *CS7*, *C119*, *C101*, and *C103*) that the possible error is well within the experimental error of the other methods. So far as the intermittency effect on the photographic plate is concerned, O'Brien (*C90*) has shown that if the number of in-

transmittencies or light increments which are to make up the total energy affecting the silver halide is greater than 150 to 200 no observable error will be involved in the sector method within the accuracy with which the other variable factors can be controlled or measured; such as the cell thickness, the concentration, the position of the diffuse edges of the absorption band (matching the negative), or the setting of the sector values.

The simplicity of the sector and diaphragm methods is one of their greatest advantages, and, even though there are a number of optical methods of ultraviolet photometry, these methods are still the most practical and most widely used procedures. In the simplest form a single rotating sector is placed in the comparison beam and the sample to be measured is placed in the other beam. Both beams are brought into juxtaposition at the slit by one of the optical methods which have been suggested (Fig. 8.6), and a series of photographs or observations is made with different settings of the sector opening. The sector opening can be graduated in degrees, percentage, or extinction (see Table IX in Appendix for the relation between these factors). In many instruments two sectors are used (Hilger, Bausch and Lomb, Gaertner), although in some a single sector with two separate segments is employed (Bausch and Lomb, Keuffel and Esser) and in other instruments only a single sector is employed (Zeiss). Table IX, "polarizing angle 45° extinction" column, is intended to apply to the optical method, in which a prism angle of 45° yields two fields of equal intensity, and at either 90° or 0° one or the other of the two beams is extinguished. The effective angle is thus 45°, which can be graduated in 100 divisions to read in percentage, or in the negative logarithm of the percentage to yield the extinction value.

$$E = 2 \times \log \tan \theta$$

(4 \times $\log \tan \theta$ if instrument has match points every 45° instead of 90°).

In sectors which are composed of two 90° segments or one 180° segment it is necessary to expand the percentage graduation system to 100 divisions for the total opening or the corresponding extinction values. If no sector of similar maximum opening is used in the sample beam it will be necessary to graduate the sector on the basis of 360° rather than 180° total opening. Most sector instruments use two sectors, one in each beam, with a sector in the sample beam of constant opening (usually one 180° or two 90° openings), and the other sector in the solvent or comparison beam which is adjustable to a maximum opening equal to the constant opening of the solution beam sector.

Not many of the modern sector or diaphragm instruments are constructed with both sectors adjustable; this, however, is quite advisable so

that the sample and comparison beams may be interchanged and thus eliminate possible instrumental errors due to alignment or graduation. Since the intermittency error becomes negligible with sufficient interruptions of the beam it often becomes desirable to remove the sector entirely from the sample beam, thus doubling the amount of light transmitted (from 50 to 100 per cent) and producing a condition similar to the

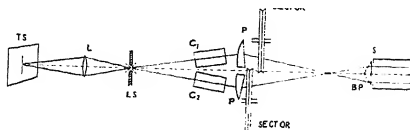


FIG. 8.10.—Hilger sector photometer. (See Chapter XII, Exercise 9 for description of parts.)

transmission of diaphragm instruments. This can be accomplished in the Hilger instrument by removing the driving belt for the sector, or in the Keuffel and Esser instrument by lowering the sector drive. This change from 50 to 100 per cent involves an increase in the extinction values of 0.3, i.e., 0.3 should be added to each value used to get the true extinction. This change permits higher values to be set with greater accuracy,

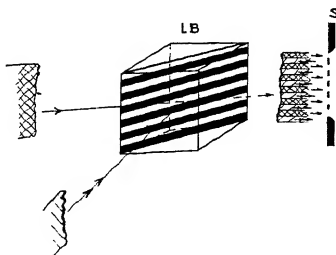


FIG. 8.11.—O'Brien photometer cube.

and shorter exposures are required for equal spectrum density (e.g., with the sample sector stopped and left open, a setting of 1.5 E on the comparison sector will give a value equivalent to 1.8 E).

A special type of sector photometer which deserves mention and which promises to speed up the procedure of photographic spectrophotometry has been devised by O'Brien (190). This instrument uses a multiple

Luhmmer-Brodhun cube with ten to twelve alternate contact faces or strips (Fig. 8.11), so that over a slit height of about 15 mm there will be

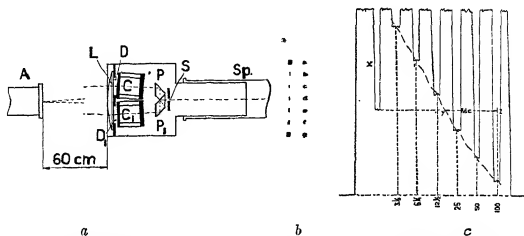


FIG. 8.12.—*a* Multiple slit photometer; C and C_1 indicate solution and solvent cells illuminated by light source (A) through lens (L) which focuses on the spectrograph prism. Rhombs (P) and (P_1) project beams through slit (S).

b Step slit.

c Microphotometer record of spectrum intensities (measured at right angles to dispersion direction) showing method of extinction determination (Moll, Burger and Rerchert—Kipp and Zonen).

that many separate strips in the spectrogram coming alternately from the transmitting and reflecting prism faces. In front of the transmitting

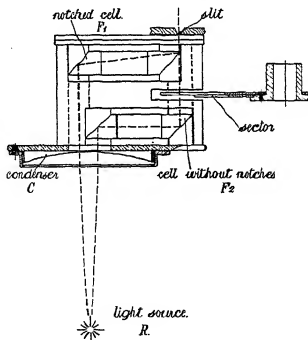


FIG. 8.13.—Optical system for echelon cells (Hilger).

face is placed a logarithmic or step sector, and in front of the reflecting face is placed a right-angle prism cell, so that both faces are illuminated

from the same source. In this manner it is possible to take the equivalent of ten to twelve separate photographs at different extinction values in one operation. There is no particular restriction on the cell size or thick-

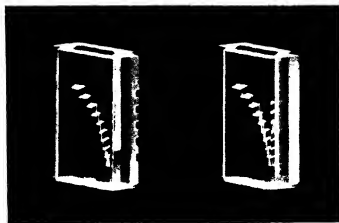


FIG. 8.14.—Echelon cells (Hilger).

ness so long as the entire prism face is illuminated. It is essential in this method to have an even and uniform illumination covering all of the two prism faces.

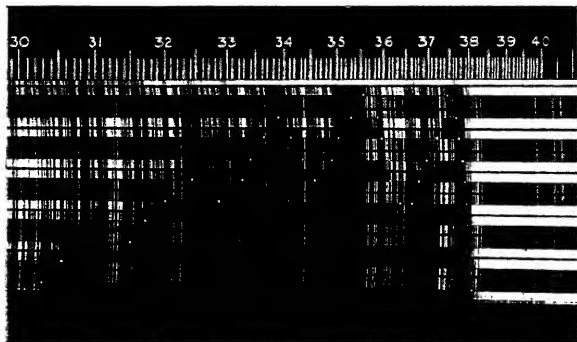


FIG. 8.15.—Photograph taken with echelon cells.

A somewhat similar device in which a number of photographs are taken simultaneously is available in the form of the Hilger echelon cells (*C116*) in which the variation in extinction is accomplished by changing

the thickness of the solution in a series of logarithmic steps. A sector is used in front of the comparison beam to reduce the transmission to known extinction values (Figs. 8.13 and 8.14). The notched echelon cell provides a very convenient and rapid method for spectrophotometric analysis, but is limited to low extinction values by the maximum cell thickness. In a single exposure ten photographic pairs can be obtained representing an extinction change from 0.0 to 1.0 in steps of 0.1 E .

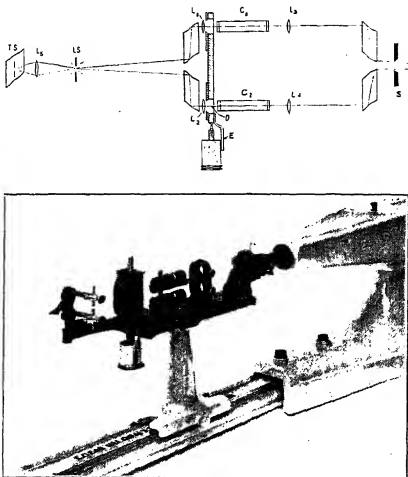


FIG. 8.16.—Hilger Spekker photometer.

HILGER SPEKKER PHOTOMETER

The rotating sector method as developed by Twyman of Adam Hilger has been the means for producing most of the quantitative data which are available today. To overcome some of the possible disadvantages of, and improve upon, this excellent contribution in apparatus development, Twyman has recently designed a diaphragm photometer known as the Hilger Spekker photometer (*C115*). In this instrument (Fig. 8.16) it is not necessary to take the light from as great an angle of view as is necessary in the Hilger sector photometer since the beam is spread by two

quartz rhombs. The beams are made approximately parallel by means of the lenses L_1 and L_2 and then pass through a fixed diaphragm and an adjustable diaphragm D . The adjustment of this rectangular diaphragm is effected by a micrometer screw with an indicating drum and guide, E . The drum is graduated in extinction values, and the diaphragm is so constructed that the higher extinction values can easily be set with accuracy. The final observations are based on the relative transmission of

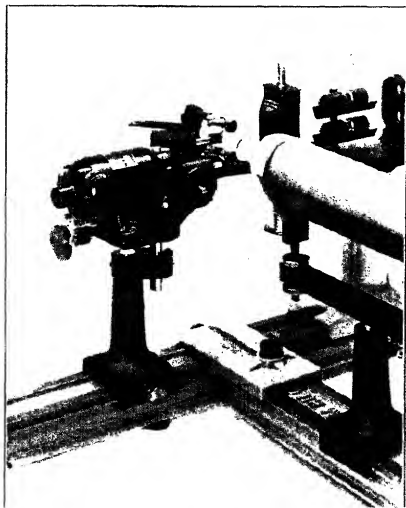


FIG. 8.17.—Rocking mirror for concentrated source (Hilger).

the fixed and adjustable diaphragms, and it is therefore essential that the cells C_1 and C_2 , for the solution and solvent respectively, should be of such a diameter that neither one masks any part of the optical beam. The two beams are brought to a focus on the slit of the spectrograph through the lenses L_3 and L_4 and are brought into juxtaposition at the slit of the spectrograph by the second pair of quartz rhombs.

Twyman has pointed out that this instrument has certain advantages over his previously designed sector photometer in that the absence of

motor-driven sector parts and interruption of the light beam removes a possibility of synchronism of the light-source fluctuations with the period of the sector so as to produce erroneous results. This error is not apparent in the use of d-c light sources or high-frequency a-c light sources such as are found in the underwater spark or a 500-cycle a-c hydrogen discharge tube. As has been pointed out in this discussion, the advantage claimed for the Spekker photometer of an increase in intensity by a factor of 2, due to the stoppage of the constant beam by a 50 per cent sector, is not a valid argument in favor of the diaphragm instrument since the constant sector can easily be stopped or removed from the path of the

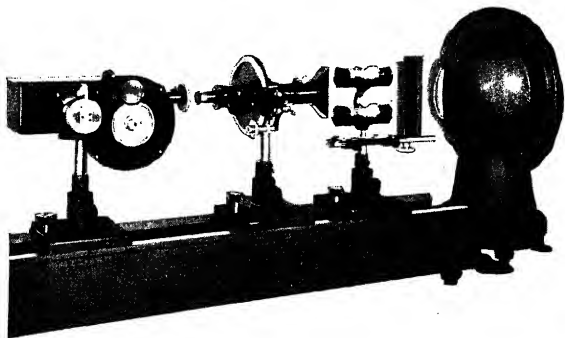


FIG. 8.18.—Spectrophotometer (Gaertner).

solution beam, and in fact some of the quantitative spectrophotometer methods use but one sector, namely, that in front of the solvent cell (Zeiss method).

The outstanding advantages of the Spekker instrument are the ease of making settings without the necessity of stopping moving parts, and the greatly increased accuracy in making extinction settings, especially at high density values. The rhomb system of light gathering so as to take the two beams from nearly the same direction from the light source permits the use of a point or concentrated light source. To permit the illumination of both rhombs where the light source is too highly concentrated or directed, as in the hydrogen discharge tube, a rocking mirror device has been designed to direct the beam alternately to the two rhombs (Fig. 8.17). This alternating or rocking mirror illumination reflector is subject to the same objection of synchronism of the reflecting motion with the

phase of the current operating the hydrogen tube or other light source. If this speed of mirror motion is set sufficiently slow to avoid the possibility of this error then one must consider the constancy and uniformity

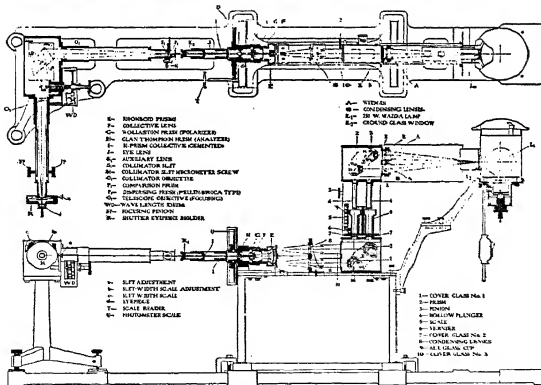
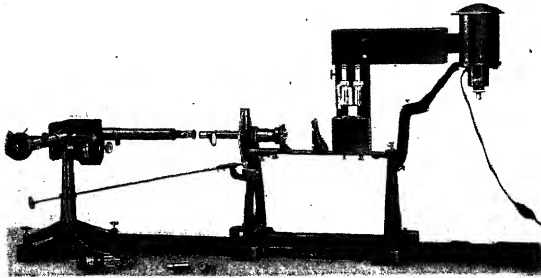


FIG. 8.19.—Spectrophotometer (Bausch and Lomb).

of the light source since only one of the two beams of the photometer is illuminated at a time.

The rhomb system for gathering the light from approximately the same angle of view is a distinct advantage in that it makes adjustment

of the position of the light source much easier. It is equally possible, of course, to construct a sector photometer with a rhomb system of illumination to effect this same improvement in ease of adjustment (as in the Bausch and Lomb sector photometer). The Spekker photometer as well as some of the sector photometer methods (including the Bausch and Lomb instrument) do not permit the reversal of the cells in order to correct for possible instrumental or alignment error.

Instruments involving an optical method (polarized light) are usually designed for visual measurements, although nearly all of them have photographic as well as visual attachments and some of them are of quartz construction and designed for ultraviolet operation. In these instruments the beams from the sample and comparison are polarized at right angles

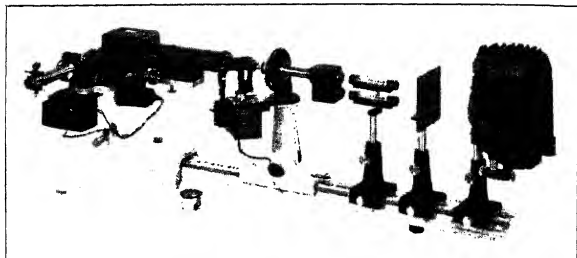


FIG. 8.20.—Spectrophotometer (Hilger).

to each other by passage separately through two Nicol prisms at right angles, or at an angle through a common Wollaston prism, so as to produce two adjacent beams, which are then passed through the analyzing prism (a Nicol or other polarizing prism) by which the two beams can be brought to the same intensity (Figs. 8.18, 8.19 and 8.20). In some of these spectrophotometers, the polarizing photometer is placed between the dispersing system and the operator or photographic recording means (König-Martens); in others the photometer device is placed between the light source and the spectrometer slit (Hilger, Bausch and Lomb). In most of these instruments the disk of the analyzer Nicol or other polarizing prism is graduated directly in extinction values, although some are graduated in percentage transmission or even in angular degrees. For purposes of conversion of either of these last two values into extinction values a special table has been prepared (Table IX, Appendix).

ILLUMINATION

The study of the absorption of light involves certain considerations that are not present in emission spectra analysis. The broad nature of most of the absorption bands with their rather diffuse edges makes qualitative analysis through the determination of band positions almost impossible except in a few compounds such as the rare earths or hemoglobin. This restriction means that in nearly all applications and measurements of absorption spectra it will be necessary to determine not only the position of the absorption band but also its intensity and shape. With the exception of a few compounds that are photosensitive, there will be no apparent loss of the absorbing substance on extended exposure, and hence an accurate determination of the amount of absorbing substance can be easily accomplished through a measurement of the percentage of light absorbed by the sample. It is obvious that for the determination of absorption spectra the most desirable form of illumination would be one of a heterogeneous character (continuous spectral radiation) such as is produced from a black-body radiation of dissociation spectra. For observation in the visual spectrum, the near ultraviolet and infrared, the incandescent tungsten bulb is an ideal source of illumination in view of its cheapness and the constancy with which it can be controlled. The availability of constant, heterogeneous light sources in absorption spectrophotometry permits the application of other than photographic or integrating methods of observation. It is also possible to increase the light intensity without altering the ratio or percentage absorbed, so that a small slit width can be used on the spectrometer and still sufficient light will be passed through to give an observable effect on a photosensitive device such as a photronic cell, thermopile, or photoelectric cell. Heterogeneous spectrum sources are not an absolute necessity, and in many cases where high light intensity of spectral purity is desired such sources as a mercury lamp will give essentially monochromatic radiation which can be separated by a rather low-dispersion large-aperture spectrometer, or even by filters of colored glass into its monochromatic emission bands. A disadvantage of such lamps is the difficulty encountered in attempting to control them to the same accuracy of radiation intensity as can be applied to the tungsten lamp. (See Fig. 3.35.)

The incandescent tungsten arc (Pointolite lamp) has also been used in spectrophotometric measurements, but is not as satisfactory as condensed-filament or ribbon-filament lamps. For the near ultraviolet it is possible to obtain tungsten-filament lamps with Corex glass envelopes, or, on special order, it is possible to obtain such bulbs with quartz envelopes or windows. Since the temperature of the filament controls the

relative amounts of radiation in the various spectral regions, it is quite obvious from these data (*C50*) (Fig. 8.21) that for extreme ultraviolet illumination it will be necessary to burn the lamp at an overvoltage such as is applied to a photoflood bulb. This will shorten the life of the lamp

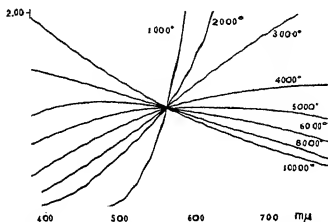


FIG. 8.21.—Relative distribution of energy radiating from a black body at indicated temperatures (*C50*).

but will increase the ultraviolet radiation by a considerable amount (Fig. 8.22).

PHOTOELECTRIC SPECTROPHOTOMETERS

A number of spectrophotometers have been designed to operate by photocell, thermopile, or photronic cell with which one may measure in

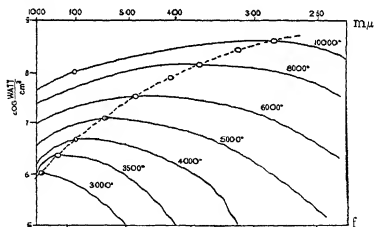


FIG. 8.22.—Total energy from a black-body radiator.

rapid succession, using a constant light source, the unknown and comparison samples so as to determine the relative transmission at a given wavelength. Repeating such measurements at a series of wavelength or frequency values will supply the necessary data to plot an absorption curve. There may be some question as to the relative sensitivity of the

photocell or other sensitive device to radiation of differing intensity, so it will be necessary to calibrate the photocell over a range of known intensity differences or incorporate into the instrument some photometer wedge, screen, or other device to reduce the intensity of the comparison

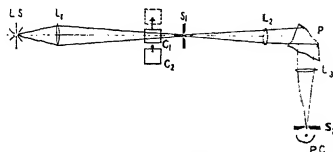


FIG. 8.23.—Hogness photoelectric spectrophotometer (*C69*).

beam to that of the unknown sample (Fig. 8.23). Some photoelectric instruments operate on a null basis, using either two separate cells or a means of alternately exposing the same cell to the sample and comparison beams (Fig. 8.24) (*C69*, *C60*, *C54*). The difficulty of obtaining photocells

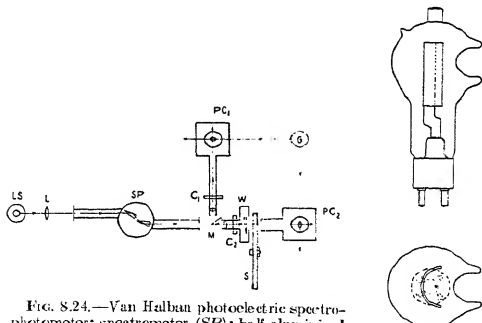


FIG. 8.24.—Van Halban photoelectric spectrophotometer; spectrometer (*SP*); half-aluminized mirror (*M*); cells (*C1*) and (*C2*); photometric wedge and sector (*W*) and (*S*); photocells (*PC1*) and (*PC2*)

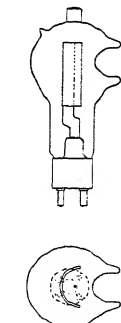


FIG. 8.25.—Thin window photo cell (Westinghouse).

with uniform response over the spectral range makes it more desirable to use a null method involving but one cell, where observations with an accuracy which exceeds the possible cell differences are required. For ultraviolet measurement, a quartz photocell or thin window glass cell (Fig. 8.25) may be used; in the visible, photronic cells, photocells, and ther-

mopiles can be used; in the infrared the usual sensitive device is the thermopile, although one may use a photocell out to about 1500 $m\mu$.

With an electrical value as a measure of the intensity differences in the two beams, it becomes quite a simple matter to connect the electrical circuit to a recording voltmeter such as the Leeds and Northrup Micro-max recorder, and to gear or calibrate the motion of the paper to the spectrometer so as to record the absorption spectra in graphical form (*C1*). One of the most successful of these coupled recording devices and one which is commercially available is the Hardy spectrophotometer which is produced by the General Electric Company (*C60*, *C86*) (Figs. 8.26 and 8.27). This instrument uses two dispersing prisms much as the

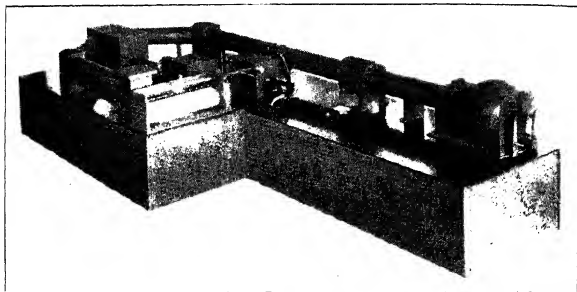


Fig. 8.26.—Recording spectrophotometer (Hardy-General Electric [*C60*, *C86*]).

van Cittert double monochromator, in which the prisms and two end slits in the instrument are fixed in position and the dispersion is accomplished by placing a slit at the focal point between the two prisms. In the Hardy spectrophotometer an aluminized mirror serves as one side of the slit and the two prisms are placed so as to have their spectral focal points approximately in the same plane. A single motion of this mirror slit thus changes the spectral region and at the same time corrects for the change in focal length of the lens system used for the different wavelength values.

In the comparison of the beam intensities one may manually change the cell from one beam to the other (which may be accomplished by interchange of the sample and comparison cell), or, by means of an optical device, bring into the field of view through the same dispersing system the light from both sample and comparison beams. The Hardy instru-

ment utilizes the double polarizing prism system similar to the König-Martens photometer (Nicol and Wollaston prism) in reverse order, in that the light starts from a single beam through the Wollaston prism and is split into two beams, rather than starting as two beams and being brought together as one beam consisting of two oppositely polarized components. The two components which are obtained in the Hardy instrument are, as in the König-Martens photometer, polarized at right angles, and a rotation of the Nicol prism enables the operator to match the two beams to equal intensity. The separation of the two beams permits the introduction of the samples to be tested, and after passing through or being reflected from the samples (depending on whether

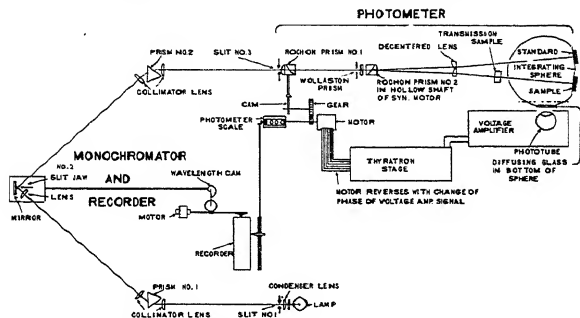


FIG. 8.27.—Diagram of recording spectrophotometer (Hardy-General Electric)
[*CoO*]

transmission or reflection measurements are desired) the two beams are again brought together by optical means and are focused on the same photocell or eyepiece. In the comparison of the two beams electrically, one may measure the two beams separately with two photocells, as has been suggested, by rapid manual alternation, the use of split prisms, or partial transmitting mirrors, or one may focus the two beams on two halves of a split field photocell (which is made especially for the matching of two fields). Such photocell amplification would involve d-c differences.

A second and very satisfactory method is the alternation of the light beams between the sample and comparison so as to produce an a-c response in the photocell if there is a lack of balance in the intensity of the two beams. This alternation effect has been successfully applied

through the use of a rotating sector to interrupt the two beams alternately, the use of a vibrating mirror to project the two beams through the comparison and sample (*CC1*) alternately, or the use of an additional polarizing prism if the original optical method involved a polarizing principle so that the two beams are already polarized at right angles to each other. The additional polarizing prism (for which purpose a Rochon prism is quite satisfactory) may be rotated in the beam so as to transmit the comparison and sample beams alternately. The use of a rapid alternating beam permits the amplification of the photocell current through an a-c amplifier which will not respond if both beams are of the same intensity. If the beams are not of the same intensity, then the phase of the alternating current will indicate the more intense beam. The control of

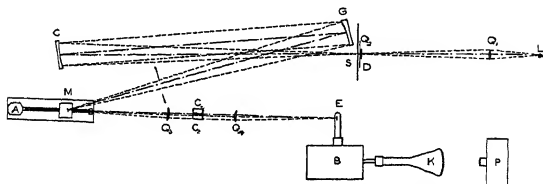


FIG. 8.28.—Diagram illustrating principle of the Harrison recording spectrophotometer; light source (*L*), log sector (*D*), slit (*S*), grating (*C*), vibrating mirror (*M*), solution and solvent cells (*C*₁ and *C*₂), photo cell (*E*) (*CC1*).

the adjustable polarizer to bring the two beams to a balance and reduce the a-c impulse can easily be effected by a motor or other device which operates on a two-field principle and depends on whether the two fields are in or out of phase as to the direction of motion of the motor armature or phase meter needle. If a motor device is used, as in the General Electric-Hardy instrument, the operation will depend upon the phase of the field current operating the synchronous motor which rotates the prism, as compared with the phase of the amplified armature circuit from the photocell. This motor power can be used to operate a recording pen and produce an automatic record of the absorption spectrum, provided that the dispersion system is coupled to the film or paper to move it along as an ordinate against the abscissa motion of the extinction record.

The success of this type of machine, especially with regard to high speed and accuracy, has prompted the extension of similar recording means to the ultraviolet region. Two such instruments have been constructed, applying quite different principles of operation and recording. One of these (Brode) uses as a dispersing system a Wadsworth-mounted

quartz prism with a screw motion provided for the lens and slit system so as to keep the monochromatic light source slit in the focal plane of the spectrum and also at the focal point of the collimating lens of the photometer so as to produce a parallel beam in the photometer. The Wadsworth-mounted prism, cut with the quartz crystal axis parallel to the base of the prism, obviates the necessity of the use of a Cornu prism since at the angle of minimum deviation of the prism there is no doubling of the image. Two photometer systems have been used on this instrument, one involving a rotating mirror sector (aluminized plates) for separation of the beam into two parts alternately, and a vane photometer principle for reduction of light intensity in the comparison beam. The two beams

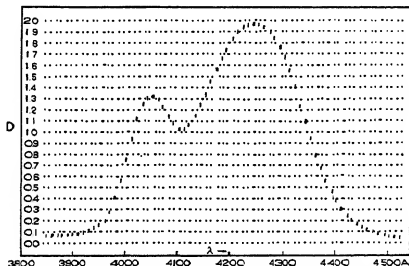


Fig. 8.29.—Form of the final photographic record of absorption spectra taken by the Harrison spectrophotometer (*C&I*).

are brought to focus on the same photocell whose amplified alternating current operated the recording pen and changed the transmission vanes so as to produce a match of the two beams, the direction of motion of the pen and vane being determined by the phase of the amplified current. Excellent curves have been produced by this method where ample light intensity was available, but for lower intensities the higher amplification resulted in out-of-phase currents owing to the cutting edge of the sector. The photometer was therefore changed to a Jobin and Yvon instrument which was designed for visual and ultraviolet spectrophotometry. This photometer uses special ultraviolet-transmitting polarizer and analyzer prisms, and by suitable arrangement of the parts is available for the determination of optical rotation as well as absorption. The availability of this machine for the graphical determination of optical rotatory dispersion curves in the visual and ultraviolet spectral regions

greatly enhances its value to the chemist. The alternation of the two beams on the photocell by a polarizing prism or screen (Hardy method) induces the necessary alternating current for the operation of the matching and recording devices.

The Harrison recording spectrophotometer (Fig. 8.28) uses a grating rather than a prism dispersing system, and hence a photometer may be incorporated as a rotating logarithmic sector in front of the slit and still give even illumination over the spectrum line at the focal point. The exit slit of the monochromator, in this instrument, is an aluminized mirror on a thin quartz strip, the width of which acts as the slit width for the system. The mirror is mounted on a vibrator which alternately sends the beam through the sample and through the comparison to focus on the same phototube (a Zworykin electron multiplier tube). The vibration of the mirror, like the rotation of the sector or prism, is synchronized with the rotation of the logarithmic sector in front of the slit, and the amplified electrical effects are recorded photographically by means of a cathode-ray tube. The final photograph appears as the absorption spectrum curve of the sample (Fig. 8.29), in which the ordinate scale appears as dots produced as a result of recording at definite positions of the logarithmic sector as the beam passes through the comparison cell. The number of these dots in a line across the record is determined by the number of settings of the thin mirror position to a different spectral region. Since the sample intensity remains constant at each frequency value, a heavy dot or dash indicates the transmission of the sample and the absorption curve is thus recorded photographically. No attempt is made to balance the two beams, but a number of unit transmission values for the comparison sample are recorded adjacent to or in juxtaposition with the transmission value of the sample which, in the end, provides exactly the same data, namely, the absorption spectrum of the sample.

LIGHT SOURCES

Within the visible, and for a certain portion of the ultraviolet, the incandescent tungsten-filament lamp provides a very satisfactory lighting source for comparison of beam intensities. For the remainder of the ultraviolet it is desirable to have a similar continuous heterogeneous source. A near approach to such a source can be obtained by sparking between uranium electrodes (an almost continuous background is produced because of the very large number of lines), or by means of a nickel and iron electrode in the arc, which is placed at right angles to the spectrograph slit so as to avoid a difference in line strength in the top and bottom parts of the spectrum.

Various forms of hydrogen discharge provide the best available sources for a continuous heterogeneous source. These may be classified as arcs, discharges, and condensed sparks. A simple arc in pure hydrogen has been found to be satisfactory, although the modification of this type as prepared by Munch seems to offer the most satisfactory continuous source which has so far been made available in the region from 350 to 200 $m\mu$ (Fig. 8.30). Hydrogen-discharge tubes have been used very extensively (C109) (Fig. 8.31) and are ideal where but a single beam of light is to be used and where an a-c effect does not complicate the measurements. Modifications of this type of tube have been constructed with quartz tubing and water cooling so as to permit the utilization of high-density currents with a corresponding increase in the intensity of illumination. The third type of source suggested is the underwater spark (Fig. 8.32). Distilled water has a much higher dielectric constant than air, so that a spark which would normally discharge across a 1-foot gap in air will require a gap less than $\frac{3}{4}$ inch under distilled water. No metal lines are produced except at the neighborhood of the electrodes, and an excellent continuous spectrum of high intensity is obtained (Fig. 8.32). This linear source, like the filament sources or the Munch arc (in the form of a slit), has a distinct advantage in that the focal length of lenses in the optical system shortens in the ultraviolet, and a linear source permits considerable shortening of the focus without loss of the image on the spectrograph slit.

The underwater spark requires a Tesla coil circuit and a specially built discharge chamber (C79). It is common practice to use tungsten electrodes, although Nichrome electrodes have been found to be equally satisfactory. Aluminum electrodes are not satisfactory since they are deformed by the spark and require continuous adjustment. Tungsten electrodes do not require adjustment more than once every three or four months of fairly steady use, and by means of a projection system (placing a light source at the red end of a spectrograph where a plate holder would normally be placed) and casting a shadow of the electrodes on a test screen, this adjustment can be quickly and easily made. The hydrogen discharge and the underwater spark, though quite satisfactory for photographic spectrophotometry, are not suitable for photoelectric

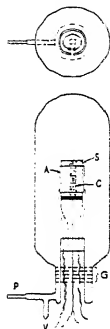


FIG. 8.30. — Munch arc in quartz bulb; palladium tube (P); graded seal (G); vacuum seal (V); alkaline earth oxide cathode (C); nickel shield with tungsten window (S); nickel anode (A) (CsS).

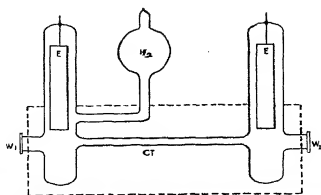


FIG. 8.31.—Hydrogen discharge tube for continuous spectra and spectrogram produced.

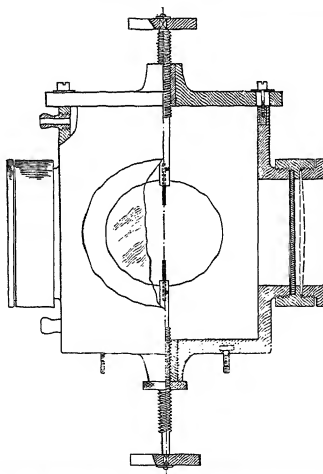


FIG. 8.32.—Under-water spark apparatus and spectrogram (C79).

photometry where measurements are made by alternating comparison of beam intensities.

As has been previously suggested, the use of tungsten filaments at overvoltage in thin glass, Corex, or quartz bulbs provides a suitable source for a considerable portion of the ultraviolet.

Homogeneous light sources, such as a mercury arc or neon tube, are of some importance in spectrophotometry where wide slits and high light intensity are desired without a sacrifice of spectral purity. The irregular position of the lines and their limited number preclude the general use of

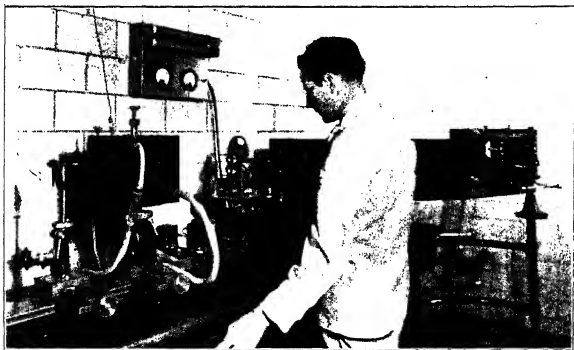


FIG. 8.33.—Spectrophotometer outfit with under-water spark, modified Hilger sector photometer and Bausch and Lomb spectrograph. (Resistance and volt-ampere indicator for arc analysis on the wall.) (Note optical bench alignment.)

such sources, but where only a low-dispersion instrument or only glass filters are available these sources become quite important in spectrophotometric measurements. For visual spectrophotometry sets of filters are available which will give monochromatic light with a mercury, sodium, or other type of vapor lamp. It is thus possible to dispense with a spectrometer and to use these filters directly with a Martens or other type of photometer for an exact determination of the spectral transmission or reflection.

CELLS

A wide variety of cells for holding solutions are available, especially where the observations are to be made in the visible portion of the spectrum and where glass can be used for the cell construction. The recent

development of fused quartz apparatus has extended many of these special cells to forms which can also be used in the ultraviolet. The Baly tube (Fig. 8.5), permitting an adjustable cell thickness, has found extensive application, especially in the earlier work in which the data were recorded as logarithms of the thickness. Accurately ground cylinders and plungers have eliminated the necessity for any gasket or rubber connection at the open end of the cylinder. A similar principle is involved in the

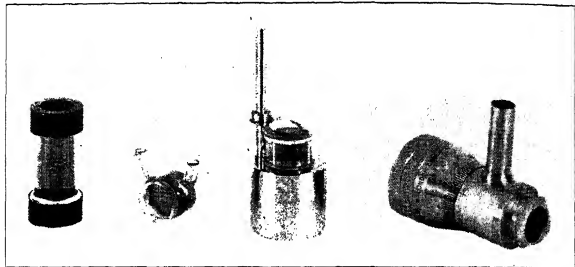


Fig. 8.34.—Cells for absorption spectra determinations (Hilger).

Zeiss and Hilger microcells (Fig. 8.34), and in the usual form of colorimeter plunger tube and cell (Fig. 8.35). This latter use requires a righting-prism in the usual optical light path so as to permit the placing of the cell in a vertical position. Such a device is incorporated in the Bausch and Lomb visual spectrophotometer and is of decided advantage where a series of rapid determinations are to be made or where it is desirable to vary the cell thickness for observation in different portions of the spectrum. In many instruments fused-glass or fused-quartz cells are available, methods having been perfected for the fusing of flat end plates onto cells without an appreciable alteration of the optical surfaces (Fig. 8.34b). For some types of observations or certain solvents, cells are available in which the plates have been cemented on with sodium silicate or some other cementing agent, but these are not always satisfactory. Where no change is to be made in the cell thickness during the observation it is desirable to use a cemented or fused cell as described above, or the type consisting of a glass tube with glass or quartz end plates held in position by slight pressure. The last type may involve a glass tube of proper length cemented into a metal tube; or long cells may have metal rings cemented on the ends. These metal tubes or rings are threaded, and a

screw cap presses the quartz or glass end plates onto the glass tube end faces. In short cells (and it should be noted that, if the concentration permits, short cells are preferable to long cells in nearly all absorption spectra work) it may be possible to have the glass tube or ring free from and not cemented to the metal tube. It will then be possible to modify the tube by the use of pairs of shorter rings to produce cells of shorter thickness than that for which the holder was originally designed. It is

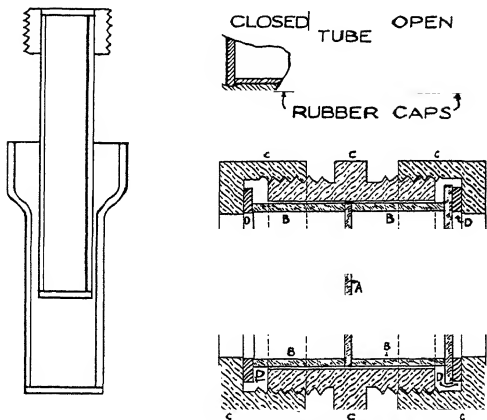


FIG. 8.35.—Diagram of absorption cell used with the Hilger sector photometer method.

a. Quartz end plate; *b.* glass rings; *c.* brass parts; *d.* rubber washers

FIG. 8.35.—Absorption cells.—*a.* Colorimeter type,
b. Tube type (Brode [6]).
c. Special jacket type (Brode [13]).

necessary, of course, to have available for this purpose cover plates of the same diameter as the glass rings so as to fit in the metal cylinder.

One of the most convenient cell types is that used by Scheibe and others, in which the end plates are held by pressure from each end and no enclosing metal tube is used (Fig. 8.36). Such holders permit the use of a large number of different cell thicknesses with the same holder. The freedom from metal parts in contact with the cell permits the use of strong acids such as concentrated hydrochloric or sulfuric acid as a solvent. In such cases it is suggested that the cell be modified by placing

two rings on each side of it so as to keep metal parts away from it. These cells when properly cleaned and filled will be found to give excellent

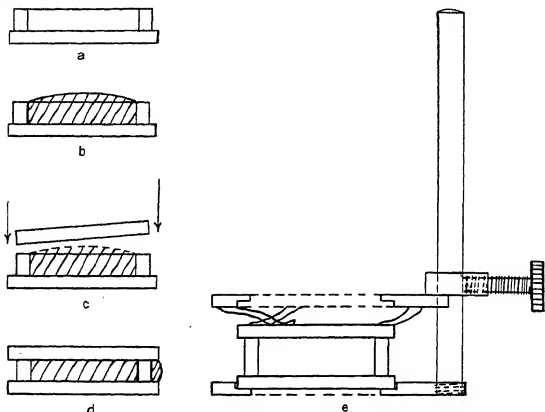


FIG. 8.36.—Method of filling cells.

service, and such solvents as diethyl ether will be held without leakage or evaporation for a considerable period of time. Accurately ground rings

can be made by grinding down rings of Pyrex tubing of the proper diameter, or complete sets of these cells can be obtained on the market. About the smallest cell thickness obtainable in this type is 1 mm, and such cell rings are, of course, very fragile. For cells of smaller thickness, rings may be made of metal sheet or foil if the sample and solvent do not attack this material (platinum or stainless steel is generally used). For accurate work where thin metal

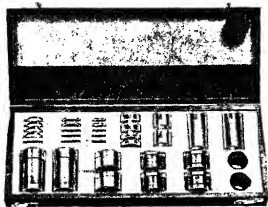


FIG. 8.37a.—Cells for absorption spectra determinations (Bausch and Lomb).

rings are not permissible, cells are available in which an indented area has been ground on a quartz plate so that it amounts to a cover plate and a fused-on ring, the second flat cover plate being all that is required to complete the cell (Fig. 8.37a).

SOLVENTS

The concentration of the compound in most solutions which are to be observed spectrophotometrically is relatively low. The absorption, if

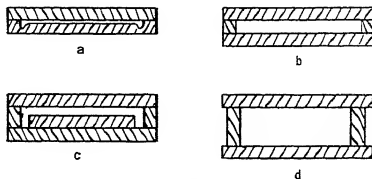


FIG. 8.37b.—Special cell types for absorption spectra determinations.

any, of the solvent will hence act as a rather sharp cut-off to limit the spectral range over which observations may be made. In Fig. 8.38 the

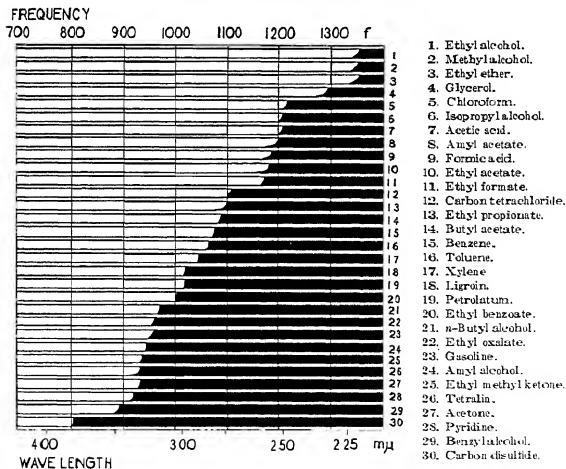


FIG. 8.38.—Absorption of commercial solvents for a 1-cm thickness. Slope of edge of band indicates gradual or sharp absorption. (Brode [C11].)

cut-off ranges of a number of laboratory solvents are indicated. It should be noted that these are not all chemically pure materials, and the cut-

off for such compounds as ligroin would indicate the presence of some impure material, in as much as *n*-hexane is transparent to the limit of the photographic gelatin plate. Many of the commercial solvents, especially absolute alcohol, ethyl ether, and ethyl acetate, may have come

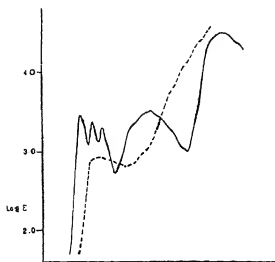


FIG. 8.39.—Absorption spectra of phthalic acid in hexane (1) and alcohol (2) (Menczel [C84]).

into contact with benzene in the process of purification, and hence one should be on guard for a series of sharp bands in the region of 1100 to 1300 f. In many observations the presence of a slight amount of absorbing matter will not interfere with the accuracy of the determination so

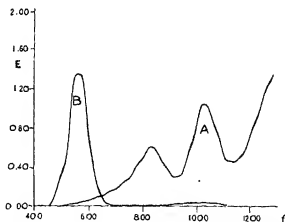


FIG. 8.40.—Absorption spectra of iodine in alcohol (A) and carbon tetrachloride (B) (Brode [C10]).

long as a solvent or comparison cell of equal thickness is used in the comparison beam of the photometer.

The available solvents, in addition to the organic compounds indicated in Fig. 8.38, include many other organic compounds such as the ethanolamines, piperidine, higher alcohols, cyclohexane, or dioxane, as

well as many inorganic compounds and solutions, such as water, ammonia, sulfur dioxide, hydrochloric acid, sulfuric acid, and water solutions such as sodium hydroxide or ammonium hydroxide. In general, it is possible to classify the solvents into two classes, polar and nonpolar. The nonpolar class includes such inactive compounds as the saturated paraffin hydrocarbons. As might be expected from their nonactive character, hydrocarbons would not appreciably disturb the vibration of the absorbing molecule, so that the absorption spectrum should more nearly approach its possible spectrum in a vapor state, in which each molecule is separated from the other vibrating molecules by space rather than by inactive molecules (Fig. 8.39).

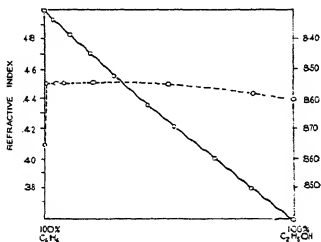


FIG. 8.41.—Effect of mixtures of alcohol and benzene on the refractive index and absorption frequency of phenylazophenol. (dotted line = frequency.) (Brode [71].)

As might be expected, polar molecules often take part in an actual chemical combination with the resonating molecule. In such cases, the larger molecule formed may have a charge and property like a polar molecule or ion, and a sharp fine-structure spectrum, such as is usually found in a nonpolar solvent, may be produced. The spectrum of iron or cobalt salts in halogen acids is an example of this effect. In the use of nonpolar solvents with resonating or absorbing molecules which have a tendency to form complexes with polar solvents, one should be very careful that the solvents are free from any of these polar solvents. Iodine, in a nonpolar solvent such as CHCl_3 , produces a sharp band at 578 f, but in alcohol, water, and potassium iodide, or other polar solvents, it produces a brown rather than purple solution with bands at 850 and 1040 f (Fig. 8.40). It is only necessary to add a drop or two of alcohol to a purple CHCl_3 -iodine solution to change it from a purple to a brown color, showing that the resonating molecule is apparently dissolved in the

polar solvent (alcohol), and that this complex or solution is in turn dissolved in the nonpolar solvent. A similar example of this solvent effect is shown in the absorption spectra of phenylazophenol in mixtures of alcohol and benzene and in mixtures of alcohol and CCl_4 (Fig. 8.41 and 8.42). These latter experiments also show that Kundt's law (absorption band of a compound is shifted in accordance with the refractive index of the solvent) does not hold. Less than 1 per cent of alcohol is sufficient to shift the position of the absorption band from 875–880 to 855 f. In view of this rather marked shift, and the known alteration in the band appearance itself with pure nonpolar solvents, it would seem advisable to

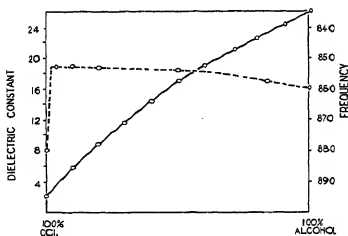


FIG. 8.42.—Effect of mixtures of alcohol and CCl_4 on the dielectric constant and absorption frequency of phenylazophenol. (dotted line = frequency.) (Brode [C11].)

be quite sure of the purity of the solvent or else to add sufficient alcohol or other polar solvent to obtain uniform and consistent results.

The effect of temperature on the absorption spectrum of a solution will be indicated in the restriction of molecular vibration as the temperature is lowered, so that at temperatures of liquid air or lower many colored compounds will become colorless. At room temperatures and higher the effects are largely those shown by polar solvents in which a reaction takes place between the chromophore and the solvent. Such effects as the change in intensity of iodine in alcohol and the pink to blue color change of aqueous or basic cobalt solutions are of this type. Another effect which is of importance, although little has been done in the field, is that of thermochromic compounds which are colorless at low temperatures and colored at high temperatures in what appears to be a reversible reaction with the chromophoric structure being induced by the higher temperature. An example of this type of compound is found in 1-(α -dimethylaminobenzyl)-2-naphthol (C26).

ABSORPTION SPECTRA (THEORY OF MEASUREMENT AND RECORDING) (A15, B20, B48, B14)

The transmission (T) of a substance is a measure of the light intensity transmitted (I) by the material as compared to the intensity of the incident beam (I_0).

$$I \quad (1)$$

The transmission factor (T) cannot be greater than unity. The percentage transmitted (transmittancy) (t) is obtained by multiplying the

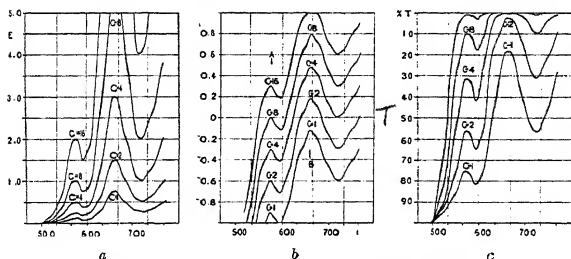


FIG. 8.43.—Graphical indication of absorption spectra.

a. Extinction (E) = $\log I_0/I$

b. $\log E$

c. % transmitted = $100 \times I/I_0$.

Note how percentage transmitted curves flatten the peaks and reduce the significance of high absorption as compared with low absorption values.

transmission factor by 100. In accordance with Beer's and Lambert's laws, the following relationship between I and I_0 is found to hold:

$$I = I_0 \cdot 10^{-kcd} \quad (2)$$

where k is a constant for the wavelength and compound under observation, c the concentration, and d the thickness of the cell. For solids of unknown concentration the c will drop out and the expression becomes

$$I = I_0 \cdot 10^{-k'd}$$

In this form the equation is essentially the Bunsen and Roscoe relation in which k is defined as the extinction coefficient in accordance with the following relations: Let I_0 be the intensity of the incident light which enters the medium, I the intensity after its subsequent passage through

the path length (d), and k , a constant depending on the medium and wavelength (Fig. 8.43a). The Bunsen and Roscoe extinction coefficient is the reciprocal of the thickness which is necessary to weaken the light to one tenth of its incident value (*C35*).

Lambert's law may be expressed thus: the proportion of light absorbed by a substance is independent of intensity of the incident light but varies directly as the logarithm of the thickness. For all substances which have been examined this law has been found to hold. Beer's law states that the proportion of light absorbed is directly proportional to the number of molecules of absorbing substance through which the light passes.

Since k , c , and d are the determining factors in recording data, and, in general, an attempt is made to match or equate light intensities, the expression of Bunsen and Roscoe is more useful in the form

$$kcd = -\log_{10} \frac{I}{I_0}$$

It is quite acceptable to write $-\log I/I_0$ as $+\log I_0/I$ although publications from the Bureau of Standards (*B14*) record kcd as a negative value and plot downwards on an ordinate basis. Curves from the Bureau of Standards are known as "spectral transmission" or "spectral absorption" rather than absorption spectra curves and have "peaks" or maxima at the bottom and minima at the top of the graph. There is a uniform agreement among practically all other workers (*B20*, *B55*, *B53*) to plot absorption spectra curves with the extinction arranged as a positive value along the ordinate of the graph form (Fig. 8.43b).

Since k in the Bunsen equation is a fixed constant independent of the concentration and thickness (c and d), and the observed value is the expression $\log I_0/I$, or its equivalent which is kcd , it is obvious that this expression is in itself a useful form, and hence we may indicate

$$E = kcd$$

where E is defined as the extinction coefficient or extinction, and k as the specific extinction, i.e., the extinction for a unit concentration and unit thickness. The same differentiation exists here between the extinction values as between other physical properties such as optical rotation or density. In optical rotation we use an expression α to indicate rotation, another expression $[\alpha]$ to indicate specific rotation (i.e., rotation per unit concentration and unit cell thickness), and, lastly, an expression $[M]$ to indicate rotation per unit molecular concentration and thickness. The same may be said with regard to weight, specific weight, and molecular weight. It would therefore seem quite logical to use some expression to

indicate molecular extinction, e.g., ϵ , which is equivalent to the specific extinction, k , multiplied by the molecular weight.

On account of the great differences in the extinction values of certain compounds, it is often more convenient to plot as ordinate values $\log k$, $\log E$, or $\log \epsilon$, so as to enable one to make a better comparison between compounds with weak and strong absorption values. It will be noticed that the recording of $\log E$ values for the same curve at different concentrations will produce a curve of the same shape but of different ordinate values (Fig. 8.43c).

Beer's law has been shown to apply to most solutions, except where some chemical reaction takes place, such as association, ionization, or dissociation, which will change the nature of the chromophore or the number of molecules in solution. In general it can be assumed to apply, and must be so assumed to apply, when quantitative analyses are made by means of extinction values in solutions of unknown concentration, unless a known series of standards has previously been prepared and the amount of increase or decrease in the absorption caused by solution action is determined for various concentrations.

In 1883 Hartley published a series of observations on the absorption spectra of determinations on an instrument used by Miller in 1860, on which the first serious investigations on absorption spectra had been made (C63). In his experiments, Hartley recorded the thickness of the solution at which light ceased to be transmitted by the solution. By increasing or decreasing the thickness of the absorbing cell he could record a quantitative indication of the absorption band shape (Fig. 8.44). The recording of the logarithm of thickness rather than the thickness (Fig. 8.3) was soon shown to give a much better indication of the absorption. Similar observations also were made keeping the cell thickness constant and gradually diluting the solution so that the absorption curve was obtained by plotting the wavelength values against the concentration or logarithm of concentration (Fig. 8.45). In many of these earlier data the curves were produced by straight lines with sharp angles, and,

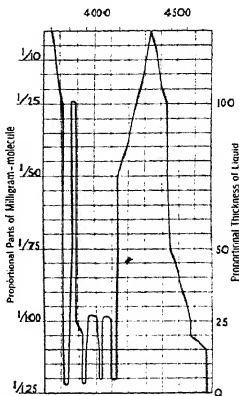


FIG. 8.44.—Absorption spectrum of benzene (after Hartley [C63]).

though they give a qualitative representation of the absorption, they do not supply sufficient accuracy to satisfy the exacting requirements of our

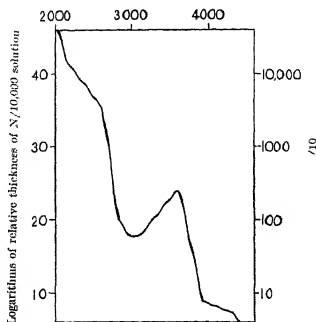


FIG. 8.45.—Absorption spectrum of α -naphthaquinone (Baly and Stewart [B54]). analytical methods of today. The curves for *p*-phenylazophenol (Fig. 8.46) as obtained by three earlier workers can be compared with

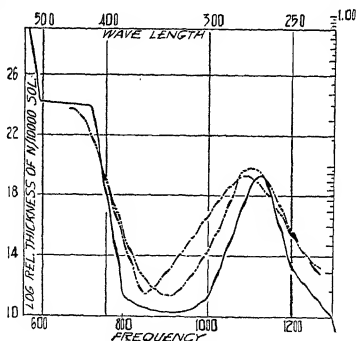


FIG. 8.46.—Absorption spectrum of phenylazophenol in alcohol (— Tuck [C111]); (--- Hantzsch [C59]); (- - - Robertson [C98]).

the same curve as obtained by the Hilger sector photometer method (C11) (Fig. 8.47), in which the accuracy of observation is considerably better than the size of the circles which indicate the points.

It is unfortunate that so much effort was put into quantitative measurements on the log thickness or concentration methods since equal photographic density is not produced at different wavelength values by equal transmission, and in the absence of a photometer or comparison series one cannot do much more than accept the wavelength position of the bands from the earlier work, and this may often be in error.

Practically all the data that have been published in the last twenty-five years have been of an accurate quantitative nature, but the lack of agreement as to the proper ordinate or abscissa often makes the exact interpretation of the data uncertain. One finds such terms as extinction, absorption, transmittancy, absorption coefficient, extinction coefficient, specific extinction, specific transmissive index, and many others as an

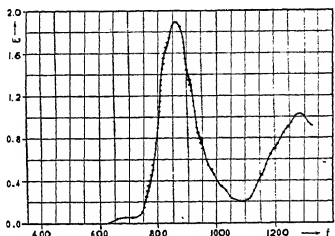
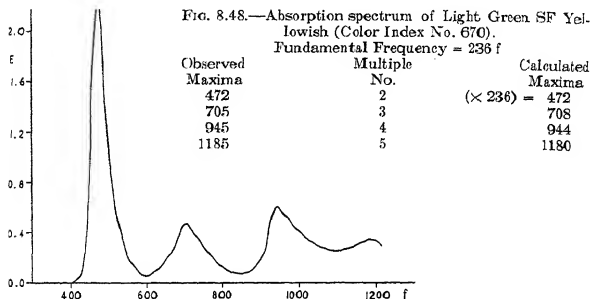


FIG. 8.47.—Absorption spectrum of *p*-phenylazophenol in alcohol (Brode [C11]).

expression for the relation $\log I_0/I$ (or kcd), and in other cases the same terms for k , $\log k$, or molecular extinction (ϵ). In the abscissa terms one finds a division of opinion between the use of wavelength or frequency and in each of these divisions a further subdivision as to whether wavelength should be expressed as angstroms or millimicrons and whether frequency should be expressed as wavenumber (cm^{-1}) or true frequency. Many workers in a desire to conform to all schools of thought have included abscissa values in wavelength, wavenumber, and frequency values on the same figure.

In the field of emission spectra, angstrom units have become so thoroughly accepted that no change or alternation seems either likely or desirable, although wavenumbers are important in this field, and one of the extended spectrum tables (Harrison, 100,000 principal lines) lists the lines both by wavelength and wavenumber. For the analysis of the spectrum into its terms and series it is essential to have the data in wavenumber or frequency rather than wavelength form. In the field of ab-

sorption spectra the presentation of data in a frequency form is essential to the complete analysis of the curves. Nearly always if two or more bands occur in the same absorption spectrum and are due to the same resonating group it can be shown on a frequency presentation that the observed bands are whole-number multiples of a fundamental frequency. One might expect this effect to be apparent for simple structures such as benzene (Fig. 7.2), but it is also apparent in complicated structures (Fig. 8.48) such as the dye Light Green SF Yellowish in which bands occur at frequency values of 472, 705, 945, and 1185 f. On the basis of 236 as a fundamental frequency, the calculated position of these bands would be 472, 708, 944, and 1180 f, corresponding to 2, 3, 4, and 5 times the fundamental frequency. It is interesting to note that in most of these com-



plex structures the first multiple of a series is missing and those immediately following the missing component are more intense than other components. Another good example of the multiple-frequency series in complex molecules is furnished by the cobalt halide series of bands in halogen acids (Fig. 7.4 and Table 7.1), in which band series are shown to exist as multiples over an extended range.

The majority of observations in absorption spectra studies are made with prismatic instruments, and, as such, the dispersion is more nearly linear on a frequency rather than a wavelength scale. Hence, on a frequency scale the slit width, error in measurement, and the like are nearly constant throughout the curve. It is recommended that all absorption spectra determinations, therefore, should be recorded in frequency rather than wavelength abscissa values. It is probable that little change can be expected in the recording of visual data used by color analysts, and many visual instruments are built with calibrations in wavelength rather than

frequency. In the recording of visual color in wavelength values it is desirable to use millimicrons ($m\mu$) rather than angstroms (\AA) since the accuracy of the measurement of wavelength values of absorption or reflection curves does not justify the greater accuracy indicated by the use of the angstrom notation. The millimicron may be defined as equivalent to 10 \AA or as 10^{-9} meter. In our systems of numerical nomenclature we use milli- to indicate a thousandth and micro- to indicate a millionth; therefore a millimicron, or $m\mu$, is a thousandth-millionth of a meter, or 10^{-9} meter. There has been a tendency to assume that micron should indicate a thousandth of a centimeter, and the expression for the unit equivalent to 10 angstroms would thus become a micromicron, $\mu\mu$, which is not a correct use of the term micron. It should be remembered, however, that in articles where the symbol $\mu\mu$ occurs it is equivalent to $m\mu$.

The conversion of wavelength values (λ) to frequency values (ν) can be accomplished easily by means of the reciprocal relations

$$\frac{1}{\lambda} = \text{wavenumber} \\ c \cdot \frac{1}{\lambda} = c \cdot \nu' = \nu = \text{frequency}$$

where c = the speed of light, or 2.99796×10^{10} cm per sec; λ = the wavelength; and ν' = the wavenumber in centimeters per second. For absorption spectra measurements the accuracy of determination is such that it is within the possible error to choose c as 3 rather than 2.99796×10^{10} , and hence, to convert millimicrons to our accepted unit of frequency, which is known as a fresnel (f), we will use the relation

$$f = \frac{3 \times 10^5}{\lambda \text{ in } m\mu} = \text{frequency } (\nu) \text{ in fresnel units}$$

or, approximately, vibrations per (second $\times 10^{-12}$). The choice of the fresnel as a unit for recording visible and ultraviolet data is very satisfactory in that the units are not unwieldy like the reciprocal centimeter values, and they provide the same numerical dimension as the millimicron within the visible range. The limits of the visible range in millimicrons are from 400 to 750, and, since the reciprocal of 400 multiplied by 3×10^5 equals 750, the fresnel units are of the same dimension for the visible spectrum, namely, from 750 to 400 f (Fig. 1.2). It follows then that any relation in one system may be equated to a similar relation in the other system, as, for example, if $500 m\mu = 600 f$, then $600 m\mu = 500 f$. The conversion from one system to another therefore is quite simple, and a table has been supplied (Table VIII in the Appendix) for this purpose.

In order to establish a more uniform system of nomenclature and recording of absorption spectra data, it is suggested that an effort should be made to record all absorption spectra curves with extinction values

plotted with an upward increase in numerical value, and that, as far as possible, frequency values be used as fresnel units and plotted with increasing values to the right. This would place the blue or ultraviolet on the right of the curve and the red or infrared at the left. To avoid confusion with wavelength notation it is suggested that these latter values should be plotted with lower numbers on the right so that, as in the frequency curve, the blue or ultraviolet will be on the right and red or infrared on the left.

The author admits that he has not always followed with exactness the above suggestions of recording spectrophotometric data either in this book or in his published papers. The data published in previous papers have been arranged in part to conform with the requirements of the laboratory in which the work was done. It has been felt worth while in this book to introduce some of the variations which are encountered in the literature so as to indicate methods and types of presentation of spectrophotometric data. In general, however, the suggested system has been followed, and it is hoped that eventually a more uniform system of spectrophotometric nomenclature and presentation may be adopted by the workers in this field.

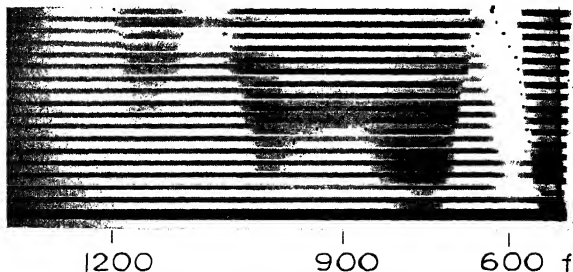


Fig. 8.49a.—Absorption spectrum of 2,5-dichlorophenylazo- β -naphthol (conc. = 0.216 cg per 100 cc, cell = 0.5 cm). N. Hilger sector photometer method with under-water spark illumination.

DETERMINATION OF ABSORPTION SPECTRA

In the determination of absorption spectra by visual means, there are usually two variable adjustments in the measurement; one may vary either the wavelength (or frequency) value, or one may vary the extinction value in order to determine a match point. In the ultraviolet instruments and other recording types, one of these two values is usually fixed in advance and a series of observations for match points are made by changing the other factor. In the sector or diaphragm photographic

methods the sector or diaphragm is set for a definite extinction value and the wavelength is varied by taking a complete spectrogram (200 to 700 $m\mu$) in the photograph, which is then examined for match points (Fig. 8.49). In the photoelectric method such as the Hardy, Hogness,

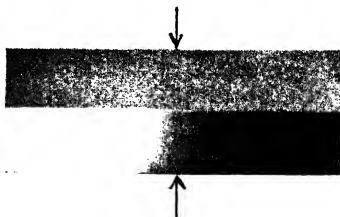


Fig. 8.49b.—Match point.

or Harrison procedures, one sets the wavelength to a definite value and then varies the extinction to a match point. Where one has the choice of method, it is advisable to set the component which more nearly parallels the absorption curve and to vary the component which more nearly

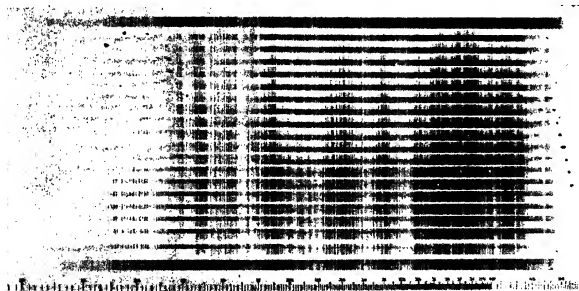


FIG. 8.50.—Absorption spectra of phenylazo- β -naphthol in alcohol. Hilger sector photometer method with Fe-Ni arc illumination. N.

crosses the curve at right angles, i.e., if a sharp curve is to be recorded one would set the extinction to definite values and would vary the wavelength, whereas if the curve is broad and flat one would set the wavelength at definite values and would vary the extinction.

For purposes of reading an ultraviolet plate it is suggested that the negative be spotted (on the glass side) at the match points (Fig. 8.50) and then the frequency values be determined by superimposing a reading plate (Fig. 8.51). A convenient form of recording these values on a data sheet is illustrated in the experimental section (Fig. 12.37).

Spectrophotometers are usually standardized or calibrated by means of known filters of glass which have been compared on other instruments. On account of the variable thickness and composition of glass it is difficult to select any glass as a standard, although curves are available on many of the Corning and Jena filters (Handbook of Chemistry and Physics, 22nd edition, pp. 1672-1685 [A22]). Three solutions which can be accurately prepared have been suggested as standards for calibra-

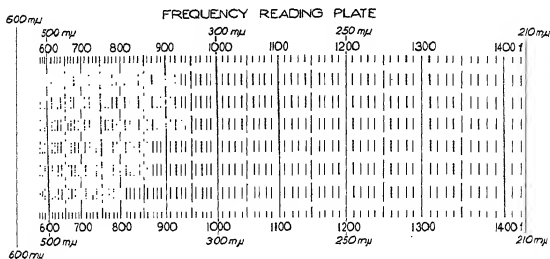


FIG. 8.51.—Frequency reading plate.

tion work. These are potassium chromate (Fig. 8.52 and Table 8.2), azobenzene (Fig. 8.2 and Table 8.1), and potassium nitrate.

A logarithm sector or graded wedge placed in front of the slit of a spectrograph which is illuminated by the light from an absorption cell, or the use of a wedge cell, will produce a qualitative indication of absorption band position and intensity, which is quite satisfactory for many purposes and is used extensively at the present time (Fig. 8.4). Mees (B39) has published an atlas of absorption spectra of a number of compounds studied by this method. By the same method the relative sensitivity of a photographic plate can be indicated, assuming a uniform light source. A comparison of the plate sensitivity curve as against that of an absorbing material observed under equal illumination conditions will give a more accurate conception of the nature of the absorption band of the material.

The methods of quantitative absorption spectrum determination require a measurable light intensity, and hence are limited to the maximum

extinction value that can be directly observed. Values of extinction greater than 3.0 are difficult if not impossible to obtain, and as a general rule extinction values should be measured between 0.5 and 1.8, in sector methods, or between 0.5 and 2.5 in diaphragm methods. For values which extend beyond these limits solutions of different thickness or con-

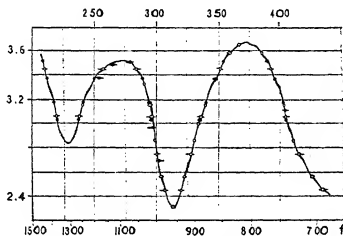


FIG. 8.52.—Absorption spectrum of potassium chromate. Molar solution in 0.05*N* KOH. $d = 1$ cm; • sector method; —○—, photoelectric method; ○, arc screen; —○—, spark screen. (Rossler-van Halban-Scheibe-Morton [*C101*, *C119*, *C103*, *C87*].)

centration should be used, and if a change in concentration seems necessary the data should overlap sufficiently to test the validity of Beer's law for the compound. The number of observations or points on the curve that it will be necessary to determine will, of course, depend upon the kind of curve. For a simple azo dye such as *p*-benzeneazophenol (Fig.

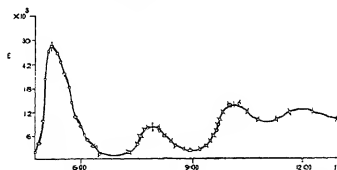


FIG. 8.53.—Absorption spectrum of benzaurin in alcoholic KOH (1 mole dye to 60 moles of KOH). (○) $c = 0.0421$ gram per liter, $d = 0.33$ cm.; (—○—) $c = 0.0421$, $d = 1.0$; (—○—) $c = 0.0421$, $d = 0.33$. (Gibbs and McNulty [*C91*].)

8.47) it can be seen that points closer than 0.1 extinction unit are unnecessary, whereas for a rare-earth glass sample (Exercise 8) it is necessary to have wavelength settings of about 2.5 $m\mu$ separation to determine the curve accurately. It is therefore of some interest and importance in the publication of absorption data in molecular or specific

extinction values to indicate the data points, concentrations, and cell thickness which were employed so that the accuracy of the observation can be judged by the reader. Some observers in the presentation of accurate data indicate such concentration and cell changes by various types of points on the specific or molecular extinction curve (Fig. 8.53). In general this is not necessary if concentration ranges and observational intervals are indicated.

LITERATURE

Practice of Absorption Spectrophotometry." F. Twyman and C. B.

Measurement of Radiant Energy." W. E. Forsythe and others, (A15).

"Optische Methoden der Chemie." F. Weigert (A73).

(A59), Mees (B39), Ley (B32), Lowe (B37), S. Judd Lewis (B30), Gibson (B14).

CHAPTER IX

APPLICATION OF ABSORPTION SPECTRA DATA

COLLECTIONS OF DATA

It is not possible, in the space available, to go into any detailed discussion of the application of spectrophotometric methods to studies on the determination of structure, biochemical problems, and industrial applications that can utilize spectrophotometric methods. In contrast to developments in the field of emission analysis, the possibility of the application of quantitative methods in absorption spectra analysis was recognized at a very early date, as is evidenced by the publication of a book by Kruss (*B25*) in 1890 on quantitative spectroscopic analysis, dealing with quantitative absorption spectra methods. The nature of absorption bands, however, prevents the detailed analysis that is possible in emission spectra, and hence we have no good compilation or method of classification of absorption spectra such as we have in the Kayser, Harrison, and other emission tables. The number of elements available has a finite limit, but there appears to be an unlimited number of absorbing resonators available in organic and inorganic molecules, so that an altogether different problem is faced in the classification and cataloging of absorption spectra data.

Several collected lists of organic and inorganic compounds, whose absorption spectra have been recorded, have been prepared. The usual classification has been alphabetical, although in some cases the compounds have been arranged according to chemical character. In many cases curves or band positions and extinction values have been included. Among such collections are the following:

1. Baly, E. C. C., Stewart, A. W., and others, a list of compounds whose absorption spectra have been studied, covering work up to 1927. *Proceedings of the British Association for the Advancement of Science (C2)*.

2. Henri, V., and Bruninghaus, L., "*Tables annuelles de constantes et données numériques, Données numériques de spectroscopie.*" Volumes I to XII covering work published between 1910 and 1936 give about 750 pages including curves or numerical data obtained from theses and previously unpublished data (*B20*).

3. Carr, E. P., Sherrill, M. L., Henri, V., Gibson, K. S., Becquerel, J., and Rossignol, J., "*International Critical Tables*," Vol. V. A collection of data and

curves on inorganic and organic compounds. Over 3,000 organic compounds are included in a formula index, covering data to 1926 (*B6*).

4. Landolt-Bornstein "Physikalische-chemische Tabellen," edited by W. A. Roth and K. Scheel, 5th edition (1923) and three supplementary editions cover

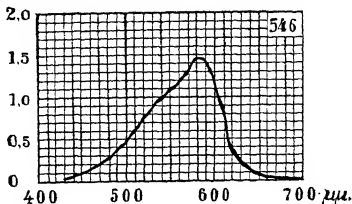


FIG. 9.1.—Portion of a page of Lasareff's "Atlas des spectres" (absorption spectrum of methyl violet) (*B26*).

the literature up to 1934. These tables include data and curves on organic and inorganic absorption spectra (*A46*).

5. Brode, W. R., "Recent Applications of Absorption Spectrophotometry," with a supplementary revision covering a selected list of references up to 1932

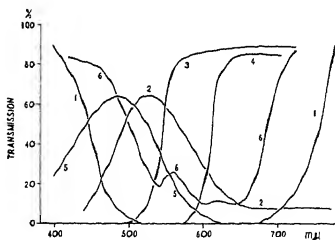


FIG. 9.2a.—Transmission spectra of glass filters. 1. Jena BG3. 2. Jena VG2. 3. Corning 351. 4. Corning 245. 5. Corning 440. 6. Corning 557.

6. Formanek, J., "Qualitative Spektralanalyse anorganischer Körper" and "Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischen Wege" (1900, 1908, and 1926). Qualitative and semiquantitative indication of the absorption spectra of a large number of inorganic and organic compounds with special emphasis on dyestuffs (*B12*).

7. Mees, E. C. K., "Atlas of Absorption Spectra." Photographic reproductions of wedge spectrograms of important dyestuffs (1909) (*B39*).

S. Jones, H. C., "The Absorption Spectra of Solutions." Qualitative and semiquantitative spectrograms of inorganic salts in solution (1909) (*B23*).

9. Lasareff, P. P., and Nedopekin, P. M., "Atlas des spectres des substances

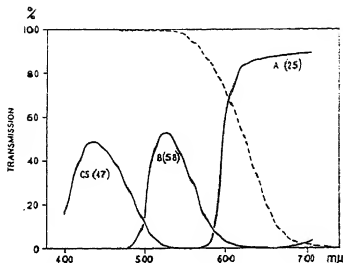


FIG. 9.2b.—Transmission spectra of gelatin filters for tricolor reproduction. Eastman Blue C5 (No. 47), Green B (No. 58), and Red A (No. 25) [*C129*]. Dotted line indicates spectral sensitivity of panchromatic emulsion.

colorantes." Quantitative visual spectrophotometric measurements on 746 organic dyestuffs, including curves and numerical data (1927) (*B26*). (Fig. 9.1).

10. Ellinger, F., "Tabulae Biologicae," Vol. XII (1937), a collection of absorption spectra curves of natural products (proteins, sugars, acids, etc.) (*B10*).

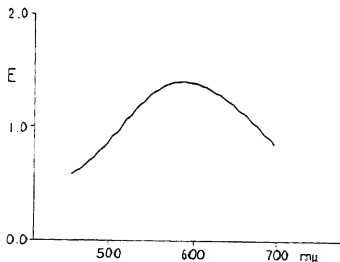


FIG. 9.3.—Iodine color with starch.

For a discussion of the application of spectrophotometric data, good general review articles are to be found in the section by Ley (*B33*) in Vol. XXI of the "Handbuch der Physik," the sections by Ramart-

Lucas (*B46*) and Lecomte (*B28*) in Vol. II of Grignard's "Traité de chimie organique," the section by Scheibe (*B49*) in Vol. IX of the "Hand- und Jahrbuch der chemischen Physik," and Twyman and Allsopp (*B53*) "Practice of Spectrophotometry," as well as the general references indicated in the bibliography. In connection with compounds of a biological nature there have been a number of compilations of absorption spectra data and methods such as those found in Heilmeyer's "Medizinische Spektrophotometrie" (*B18*), Schumm's "Spektrochem-

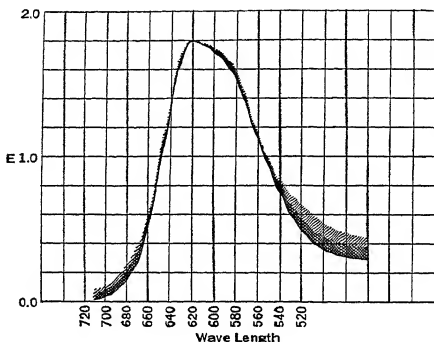


FIG. 9.4a.—Spectrophotometric curves for Agalma Black 10B (Brode [*C77*]). The inside line is the curve for the pure dye (10 mg per liter, thickness of solution 2 cm, temperature 25°C, in acetate buffer solution, pH 5.0). The curves of the 23 commercial samples lie within the shaded area, the majority of them within the heavily shaded area.

ische Analyse natürlicher organischer Farbstoffe" (*B50*), or the compilation by Ellinger on the absorption spectra of natural products (proteins, sugars, etc.) in the "Tabulae Biologicae," Vol. XII (*B10*).

Transmission curves of colored glass and light filters have been listed in the publications of the Colorimetry Section of the Bureau of Standards (*C129*) and in manufacturers' publications, especially those of the Eastman Kodak Company, Corning Glass Company, and Jena Glass Works.

QUANTITATIVE ANALYSIS

In the application of absorption spectra methods to quantitative analysis one may measure the extinction coefficient directly if the compound to be examined contains a resonating group and is free from other

resonating substances which produce absorption at the wavelength for the absorption band of this compound. In some cases where impurities prevent the direct determination one can take advantage of reactions of the resonating compound for which analysis is to be made, i.e., some other compound or reagent may be added which will produce a colored reaction whose intensity will give a direct measure of the quantity of the resonating compound that is present (Fig. 9.3).

In many dye laboratories the quantitative determinations of the amount of dye in a sample are made by the spectrophotometer, which

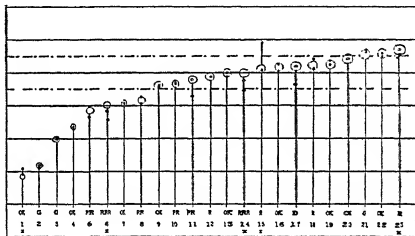


FIG. 9.4b.—Strength of commercial samples of Agalma Black 10B.

- strength by dyeing test.
- titanous chloride titration.
- spectrophotometric method.

Above the sample number is given the "shade" of dyeing as compared with Sample 13.

OK = same as 13.

D = duller.

G = greener.

X = foreign sample.

R = redder.

Note that in all cases where the spectrophotometric value is decidedly in variance with the other methods there is also a decided red or dark shade in the sample indicating impurities. (Brode [C7].)

gives an indication of the quality as well as the quantity of dye present. In this method the presence of salts or other nonabsorbing compounds will not interfere with the determination (Fig. 9.4). Slight amounts of colored impurities in a dyestuff can be detected and often identified both qualitatively and quantitatively by a study of the subsidiary dyes present. In a study of the commercial dyestuff, Agalma Black 10B, it was found that the impurities were concentrated in the mother liquor so that the identification could be made from the residual solution after a 16 per cent dyeing (Figs. 9.5 and 9.6).

The amount of dye or other substance, in accordance with Lambert's

and Beer's laws, can easily be determined from the known thickness and extinction values by means of the following formula:

$$c = \frac{\log I_0/I}{kd} = \frac{E}{kd}$$

From the known extinction coefficient (k) of the pure compound and the observed extinction (E), it is possible to calculate quite accurately the concentration (c) of the absorbing substance. This method is extensively used in the analysis and standardization of commercial dyestuffs and colorimetric reactions, without the necessity of purification or

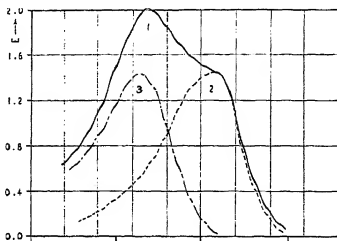


FIG. 9.5.—Absorption spectra of:

- (1) Mother liquor from a 16 per cent dyeing of a commercial sample of Agalma Black 10B whose shade was rated as RRR by dyeing tests.
- (2) Agalma Black 10B spectrum.
- (3) Impurity spectrum (Brode [C7]).

separation from other nonabsorbing materials, such as mineral salts, which are usually present.

In the quantitative estimation of vitamin A it has been shown that fish oils do not contain absorbing substances, other than vitamin A, which show an absorption band at 328 $m\mu$. It is therefore possible to estimate accurately the amount of vitamin A in a sample by a determination of the extinction coefficient of a known concentration and thickness of the oil sample. Since the compound, vitamin A, is still unknown from the standpoint of molecular size and composition, it must be assigned a specific extinction value for quantitative comparison. It has been agreed to use the factor,

$$E_{1\text{ cm}}^{1\%} \times 2200 = \text{IU}$$

which indicates that a 1 per cent solution of the oil in a 1-cm cell will contain per gram, in its original oil sample, the number of international units

equivalent to its extinction multiplied by 2200 (see experimental section page 278).

The methods of quantitative spectrophotometric analysis have been in practice for some time, as indicated in the "Manual on Quantitative Spectroscopic Analysis," published by Kruss (*B25*) in 1890 and revised in 1909. It is obvious that the use of spectrophotometric methods should be of considerable advantage in the examination of colored liquids and especially in the quantitative estimation of a colored impurity in a solution which is originally colored. Two examples of this type might be mentioned: (a) the determination of the pH concentration of a colored solution, and (b) the determination of the blood volume of a patient. In the second determination, a dye such as T-1824 (*o*-tolidine diazotized and coupled to 1-amino-8-naphthol-2,4-disulfonic acid), which has an absorption band at $505\text{ m}\mu$, a point of maximum transmission of the blood solution (Fig. 9.7), and which is not rapidly absorbed in the system, is injected in a known quantity into the blood stream. After a fixed time a blood sample is withdrawn and the amount of dye determined spectrophotometrically by setting the wavelength drum of the spectrophotometer at the absorption band position for the dye and measuring the extinction. From this value one subtracts the known hemoglobin absorption at this wavelength, and from a previously prepared standard the amount of dilution can be estimated, and hence the blood volume determined.

The spectrophotometer has been extensively used in inorganic as well as organic analysis, and one finds it almost indispensable in the purification of the rare earths, where the total color of the salt, as indicated by the area included in the absorption band, is low, but where the very intense nature of the absorption bands permits an accurate estimation of the amount of element present in a very dilute solution. Another great advantage of the spectrophotometric method of analysis is the small

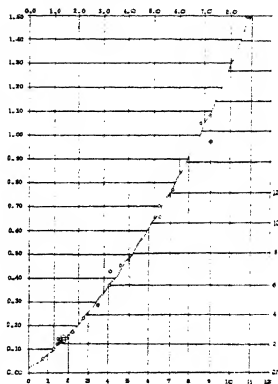


FIG. 9.6.—Relation between amount of 1-amino-8-naphthol-3,6-disulfo-7-azobenzene present in original sample and in solution after a 16-per cent dyeing (Brode [C7]).

amount of material required for analysis. By the use of micro absorption cells (Fig. 8.37) it is possible to make accurate observations on less than

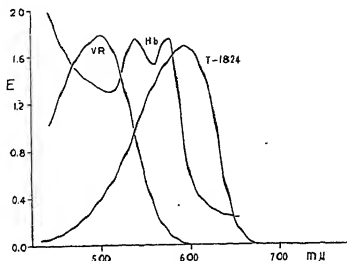


Fig. 9.7.—Absorption spectra of hemoglobin (Hb) and dyes used for blood volume determinations (T 1824 and Vital Red).

a cubic centimeter of solution, and to estimate the amount of dye in this solution when it may contain less than 0.01 gram per liter of original solution. The spectrophotometric method can be used not only to de-

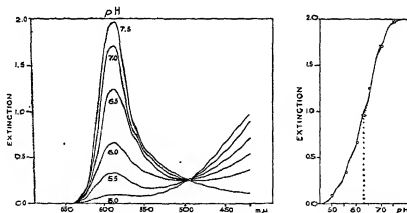


Fig. 9.8.—Spectrophotometric determination of hydrogen ion concentration.

a. Absorption spectra of bromocresol purple at the indicated pH values. (Note isobastique point at 498mμ.)

b. The dissociation curve calculated from the extinction and pH values. (Dotted line indicates dissociation constant for the indicator.) (Brode [C6].)

termine the presence of a small amount of a compound but also to measure the purity of a compound when the possible impurities may be colored substances.

GENERAL APPLICATIONS

An important field of application of spectrophotometric methods is in the determination of conditions of state such as hydrogen-ion concentra-

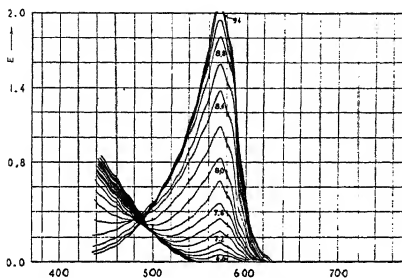


FIG. 9.9a.—Spectrophotometric determination of hydrogen-ion concentration; simple indicator (cresol red).

tion, oxidation and reduction potential, the equilibrium between tautomeric forms, and the measurement of reaction rates. The following

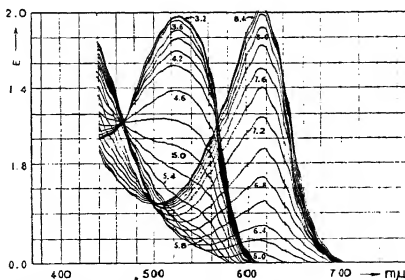


FIG. 9.9b.—Spectrophotometric determination of hydrogen-ion concentration; mixed indicator (methyl red + bromothymol blue).

examples should illustrate the method of application and may suggest similar uses. In a study of indicators (*C6*) it has been shown that the

change of pH value of the solution results in a change in intensity rather than wavelength shift of the absorption band, thus indicating the elimination of one resonating system and the formation of another. This change from one system to another is inversely proportional to the relative extinction coefficients, and hence there will be a point (Fig. 9.8) where the extinction curves should have a common value at any pH concentration. Such a point is known as an isobastique point, and the ratio between the extinction at this point and the extinction at the ab-

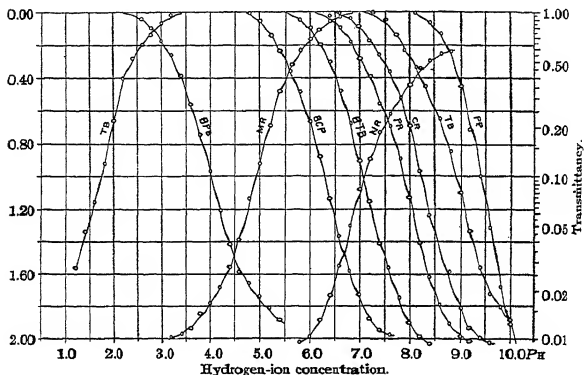


FIG. 9.9c.—Spectrophotometric determination of hydrogen-ion concentration; relation between the extinction coefficient of band maxima and pH of solution for the following indicators: thymol blue (TB), bromophenol blue (BPB), methyl red (MR), bromocresol purple (BCP), bromothymol blue (BTB), neutral red (NR), phenol red (PR), cresol red (CR), and phenolphthalein (PP). (Brode [66].)

sorption band maximum will provide a means of indicating the pH concentration of the solution which will be independent of the concentration of the indicator used.

In the determination of reaction rates and tautomeric equilibria, one may ascertain the degree of hydrolysis, association, dissociation, enolization, etc., by the measurement of the absorption spectra of compounds that produce different spectra before and after the reaction occurs (Fig. 9.10). The existence of free keto and aldehyde groups in sugars, the conditions in tautomeric equilibria between the enol and keto forms,

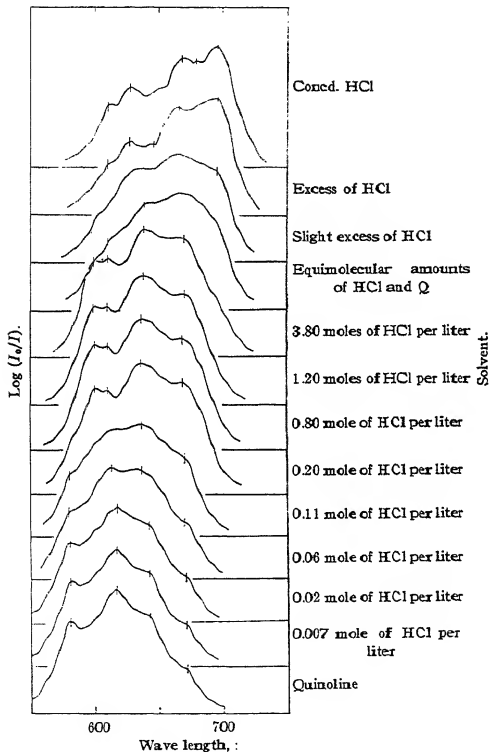


FIG. 9.10.—The change from the "Py-Q" (pyridine-quinoline) system, through the "intermediate" system to the "HX" (halogen acid) system, caused by the addition of hydrochloric acid to a solution of cobalt chloride in quinoline. (The curves in this figure are only a few of the some 50 curves, observed at various quinoline-hydrochloric acid concentrations. They have been chosen to show characteristic stages or transition points in the change of the absorption systems. The concentrations of cobalt chloride in all solutions were approximately 0.0043 mole per liter.) (Brode [C16].)

the formation of coordination complexes and chelated rings (Fig. 9.11), and the existence of intermediate compounds in a series of reactions can be indicated by spectrophotometric methods. Dimroth has shown the application of time or reaction rates to the irradiation change in certain sterols (C43) (Fig. 9.12). Brode and Magill have made a

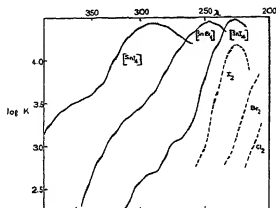


FIG. 9.11.—Coordinated tin-halogen complexes. (See Table 9.1) (Fromherz and Walls.)

similar time extinction study of the antimony trichloride reaction with vitamin-A-containing oils (C27) (Fig. 9.13) and have demonstrated the feasibility of rapid observations on a fading solution to determine the reaction rate and, by extrapolation, the theoretical initial extinction value.

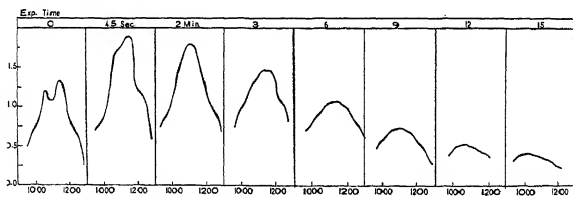


FIG. 9.12.—Effect of irradiation on sterols (Dimroth [C43]).

The interrelation between absorption spectra and refractive index or optical rotation is indicated by the formulas for the calculation of these effects, in which the wavelength or frequency of the absorption band is an important factor. In the study of rotatory dispersion of asymmetric organic and inorganic compounds, it has been possible to analyze the

absorption spectrum and the rotatory dispersion curve obtained, so as to indicate the portions of the molecule that are responsible for the various

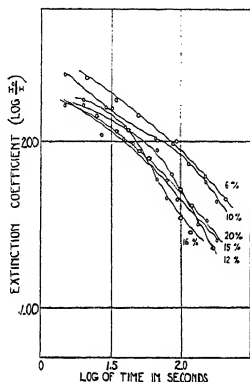


FIG. 9.13.—Change of extinction coefficient values (608 $m\mu$ band) with time, in the $SbCl_3$ -vitamin A color reaction for various concentrations of cod-liver oil. The concentration of $SbCl_3$ in these solutions was 18.5 per cent (saturated). The extinction coefficient values have been reduced to equivalent oil concentrations. (Brode and Magill [37].)

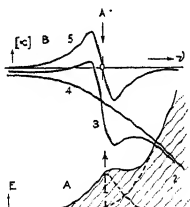


FIG. 9.14.—Relation between optical rotation (B) and absorption (A). Observed rotation (3) is resolvable into curves (5) and (4). Curve 5 is associated with the absorption center of absorption band (1) and is based on the Natanson-Drude equation with an inflection at 0 rotation at the frequency of the absorption band.

effects which add together to produce the observed effect (Figs. 9.14 and 9.15).

PREDICTION OF STRUCTURE

One of the most important uses of absorption spectra data has been in the prediction of structure and proof of synthesis. Many of the complex naturally occurring compounds are available in such small amounts, or

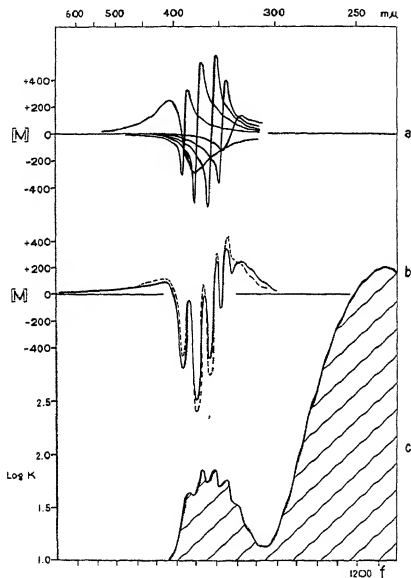


Fig. 9.15.—Absorption and rotatory dispersion of octyl nitrite.

a. Rotatory dispersion analysis based on absorption band centers.

b. Summation of rotatory dispersion analysis (dotted).

Observed rotatory dispersion (solid).

c. Observed absorption spectrum (Kuhn and Lehmann [C74]).

are so unstable, that they cannot be readily isolated from their surrounding media. It is fortunate in many of these cases that the surrounding medium does not absorb light or does so only in a limited spectral region, so that the substance often may be characterized by its absorption, and the concentration of active constituent accurately estimated (e.g.,

vitamin A). One often may predict certain structural features from the absorption spectra alone by comparison with similar compounds of known structure. Chemical tests may show the presence of certain groups, but not necessarily the position of such groups in the complex molecule. By comparing the absorption spectra of existing or synthesized compounds of known similar structure with the absorption spectrum of the unknown compound, one can eliminate certain structural possibilities (Figs. 9.16 and 9.17). Such a procedure is illustrated in the determination of the structure and in the synthesis of vitamin B₁ (C121). The final proof of structure is the synthesis of the predicted structure and its

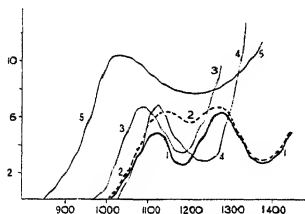


FIG. 9.16.—Absorption spectra of the ammonia cleavage product of vitamin B₁ and related pyrimidines. (1) Cleavage product. (2) 2,5-Dimethyl-6-aminopyrimidine. (3) 4,5-Dimethyl-2,6-diaminopyrimidine. (4) 5-Ethyl-4,6-diaminopyrimidine. (5) 4-Methyl-5,6-diaminopyrimidine. (Williams and Ruehle [C12].)

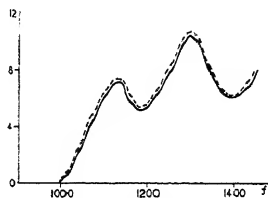


FIG. 9.17.—Absorption spectra of the natural (----) and synthetic (—) vitamin B₁ hydrochlorides [3 - (4 - amino - 2 - methyl - 5 - pyrimidinylmethyl) - 5 - (2 - hydroxyethyl) - 4 - methylthiazolium chloride hydrochloride] (Williams, Ruehle, et al. [C121]).

test, spectrophotometrically and otherwise, to show identity of the two compounds.

The prediction of structure from the absorption spectrum requires a large amount of well-worked-out data, and, even with these data available, the prediction often will be uncertain. The data might be divided into two types: (a) the influence of nonchromophoric or weighting groups on chromophores, and (b) the influence of one chromophore on another. The studies by Wulf (C123), Pestemer (C94) (Fig. 9.18), and Brode (C29) provide examples of this type of work, i.e., the influence of nonchromophoric groups attached to chromophoric groups, as shown in the change of the extinction and frequency of absorption bands. In the second class of compounds involving two chromophores in the same molecule, it has been demonstrated that certain linkages, such as the $-\text{CH}_2-$ and more especially the $-\text{CH}_2-\text{CH}_2-$ and longer chains

$(\text{CH}_2)_n$ —, act as insulating pads between the two resonating groups fail to transmit vibration from one chromophore to another (Figs.

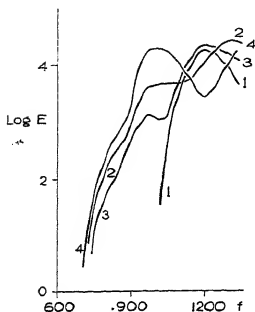


FIG. 9.18.—Variation of extinction with a change in the position of substitution. The absorption spectra of diphenyl (1), *o*-nitrodiphenyl (2), *m*-nitrodiphenyl (3), and *p*-nitrodiphenyl (4), in hexane. (Pestemer [C94].)

7.25 and 7.34). It might also be pointed out that the placing of chromophores adjacent to one another may result in an interference action and a reduction of the expected intensity (Fig. 7.25), whereas in a conjugated coupling there appears to be a multiplication effect resulting in a bathochromic and hyperchromic effect (Fig. 9.19).

Increasing the number of conjugated linkages between chromophoric resonators (Fig. 9.20) results in a continued bathochromic and hyperchromic effect, although the rate of increase becomes less (Fig. 9.21) so that there is a limit to the shift and intensity increase that can be produced by a longer conjugated chain. There also seems to be a limit from the standpoint of synthetical preparation difficulties and stability

of the highly conjugated compounds. The attachment of substituent or

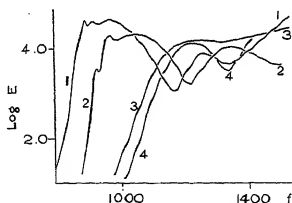
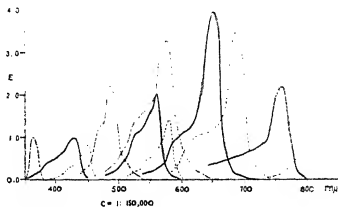


FIG. 9.19.—The influence of the separation of chromophores on the absorption spectra of compounds containing more than one resonating group. Diphenyl (4), 1,1-diphenylethylene (3), 1,2-diphenylethylene (2), and 1,4-diphenyl-1,3-butadiene (1). (Castile [C37], Brode and Magill [C27].)

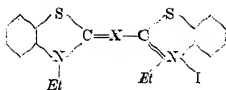
weighting groups along the conjugated chain which connect the two resonating groups may result in a marked variation in the absorption spec-

trum, much as the weighting of a vibrating string at a definite point will set up an entirely different vibrational system.

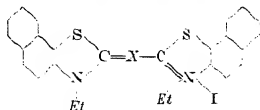
A change in the character of the resonating group, such as the replacement of sulfur by selenium (*C3*, *C49*), in a molecule in which the replaced group is an active part of the resonator, will result in a marked bathochromic and hyperchromic effect, provided that the substituting



9.20.—Absorption spectra of some cyanine dyes.



Solid-line curves from left to right indicate above formula with x equal to ($=\text{CH}-$), ($=\text{CH}-\text{CH}=\text{CH}-$), ($=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$), and ($=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-$). Dot-dash curves from left to right indicate compounds similar to the first three above but with two oxygen atoms replacing the sulfur in the molecule. Dot curves from left to right indicate the corresponding dyes with the type formula:



(All curves calculated to a solution concentration of 1 : 150,000 in methyl alcohol.) (Fisher and Hamer [*C49*].)

group is a more powerful resonator. The effect produced in this case is greater than would be predicted by increased molecular weight alone (Fig. 9.22). A decrease in the frequency of the absorption band (bathochromic effect) may be produced by changes within the molecule which may increase the conjugated path over which vibration may be transmitted, as is shown in the absorption spectra of the isomeric dibenzopyrenes (Fig. 9.23) (*C38*).

In conclusion, it may be pointed out that electronically like sub-

stances, i.e., compounds that have a similar electronic structure but differ in weighting or chromophore size, may be assumed to give similar spectra. From this statement it would seem that *p*-tolylazophenol and

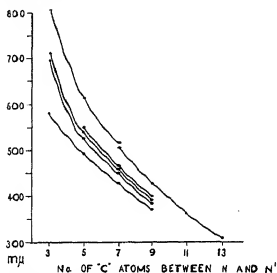


FIG. 9.21.—Effect of number of ethylene groups on the shift of the absorption maximum. (See Fig. 9.22.) (C49.)

cobalt chloride in concentrated hydrochloric acid should have an electronic or resonating structure of much the same sort, since their absorption spectra are similar. The analogous shift of absorption bands of these

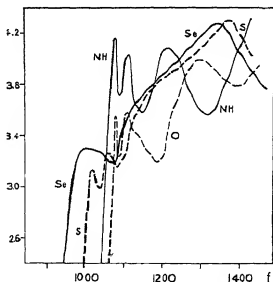


FIG. 9.22.—Absorption spectra of 2-methyloxazole and the corresponding thio, seleno, and imino analogs (Behaghel and Schneider [C3]).

compounds in neutral and basic solvents would provide additional support for this conclusion (Fig. 9.24). It may be further pointed out that nonconjugated chromophores in the same molecule produce essentially the added effects of the two separate groups, whereas conjugated chro-

mophores produce a marked bathochromic and hyperchromic effect. Increase in molecular weight will produce a minor bathochromic effect, and quite often substitution in the *para* position to a chromophoric attachment to an aromatic ring, will produce a hyperchromic effect.

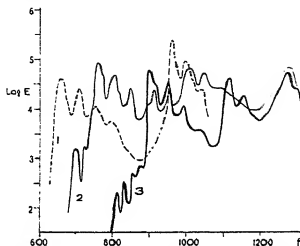


FIG. 9.23.—Absorption spectra of 3,4-9,10-dibenzpyrene (2), 3,4-8,9-dibenzpyrene (1), and pyrene (3) (Clar [C.S].)

A brief indication of the frequency values of various chromophores was given in Chapters VI and VII (see also Tables 7.3 and 10.1). However, no satisfactory solution has been obtained for a mathematical expression for the vibration effects in a complex organic molecule. It would

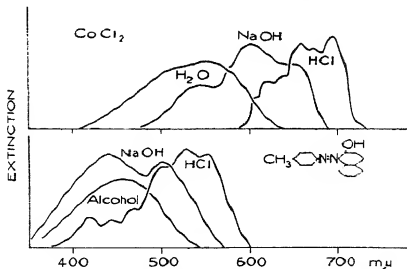


FIG. 9.24.—Absorption spectra of compounds with electronically similar chromophores (Brode).

seem that, in view of the simple character of the absorption spectrum of many of the more complex molecules, the ultimate explanation should involve a simple expression which would consider the chromophore as a whole rather than the inner and interatomic effects.

vischen Absorption und chemischer Konstitution." H. Ley
und Flüssigkeiten." G. Scheibe (*B49*).
res d'absorption." P. Ramart-Lucas (*B*
and Hormones." R. A. Morton (*B41*).

Reference

Henri (*B20*), Schumm (*B50*), Morton (*B42*), Brode and Leermakers (*B5*), Brode
(*B4*), Carr and Sherrill (*B6*), Heilmeyer (*B18*).

CHAPTER X

INFRARED AND RAMAN SPECTRA

INFRARED SPECTRA

It has been necessary to limit the spectral region which was covered in the preceding chapters, and hence no discussion of infrared and Raman spectra was included. In the classification of atomic and molecular energy

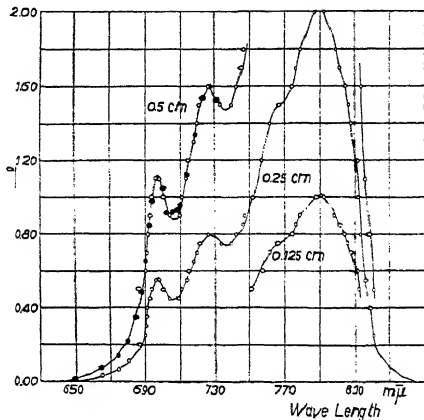


FIG. 10.1.—Absorption of cobalt iodide in concentrated hydriodic acid. 1.77 grams $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$ per liter; cell thickness, 0.125 and 0.5 cm (center curve obtained from the other two). ● = visual, ○ = photographic. (Brode and Morton [C.S].)

it has been pointed out that one could consider the total energy as the sum of the electronic, rotational, and vibrational energies.

$$E = E_e + E_r + E_v$$

In this classification, bands produced by systems in which there is a change in electronic energy are known as electronic bands and are located in the visible and ultraviolet. Occasionally they may extend into the near infrared (CaI_2) (Fig. 10.1). If ν_e (frequency change due to electronic

bands) is equal to zero, then the bands are the result of vibrational-rotational effects and are usually called vibration bands (i.e., $\nu_r = 0$; $\nu_r = 0$). Such bands owing to their low energy, occur in the infrared and seldom in the near (photographically available) infrared.

If $\nu_r = 0$, as well as $\nu_e = 0$, the only energy change will be that of rotation and the bands produced will be known as rotation bands. These

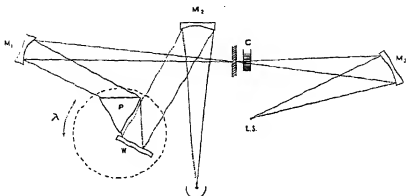


FIG. 10.2.—Infrared spectrometer, Wadsworth mounted prism (*P.W.*), concave focusing mirrors (*M*₁, *M*₂ and *M*₃), light source (*L.S.*) (Nernst glower), thermopile (*T*), and sample (*C*), in front of the spectrometer slit.

bands, owing to the very small energy change involved, will occur in the far infrared (in the neighborhood of 100μ). The pure rotation spectrum is distinctly separated from the vibration spectrum, which appears between 1 and 23μ , so that there are three distinct spectral regions of molecular absorption and emission spectra.

Our discussion so far has dealt with the electronic type of molecular spectra. The two remaining fields of

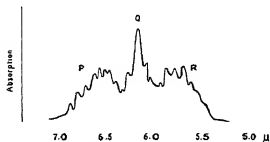


FIG. 10.3.—Absorption spectrum of NH_3 (Robertson and Fox [C99]).

spectra are not only separated in their spectral regions but also require a somewhat different technique for study. In the vibration band region, $1\text{--}23 \mu$, one can use a prism spectrometer of suitable transmission properties, such as rock salt, quartz, fluorite, or sylvite, or a grating, for dispersion, and can record the spectra by means of a thermopile or other infrared-sensitive device (Fig. 10.2).

The most suitable source of radiation is a Nernst glower.

As in the case of the electronic spectra, simple molecules in a vapor state produce spectra with a resolvable fine structure in which the *P*, *Q*, or *R* branches are easily identified. (The *Q* branch will appear only if there is an allowed vibration change with no rotation change [Fig. 10.3].) The production of rotation bands is possible only in polar molecules that

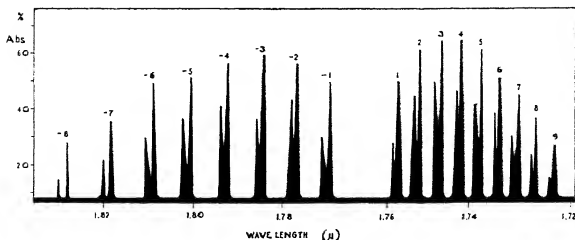


Fig. 10.4.—Isotope effect in the $3.4\ \mu$ band of HCl (Meyer and Levin [CS5]).

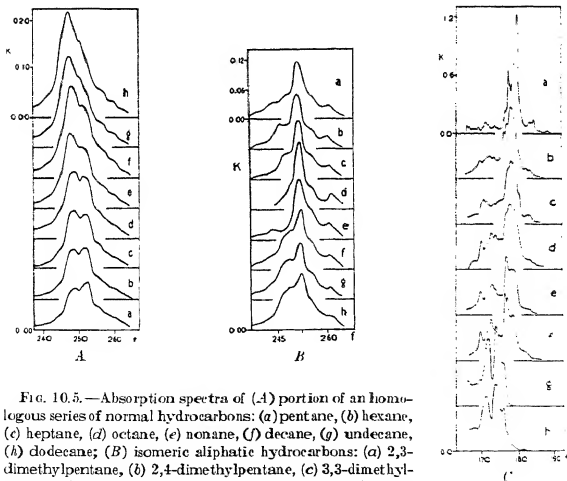


Fig. 10.5.—Absorption spectra of (A) portion of an homologous series of normal hydrocarbons: (a) pentane, (b) hexane, (c) heptane, (d) octane, (e) nonane, (f) decane, (g) undecane, (h) dodecane; (B) isomeric aliphatic hydrocarbons: (a) 2,3-dimethylpentane, (b) 2,4-dimethylpentane, (c) 3,3-dimethylpentane, (d) 2,2-dimethylpentane, (e) 2,2,3-trimethylbutane, (f) 3-ethylpentane, (g) 3-methylhexane, (h) 2-methylhexane; and (C) aromatic hydrocarbons: (a) benzene, (b) toluene, (c) ethylbenzene, (d) *o*-xylene, (e) *m*-xylene, (f) *p*-xylene, (g) cyclohexane, (h) methylcyclohexane. (Liddel and Kasper [C78].)

possess an electric moment when at rest; hence symmetrical molecules such as chlorine would not be expected to show such bands. Most of the work that has been done in infrared spectroscopy has been in the region of

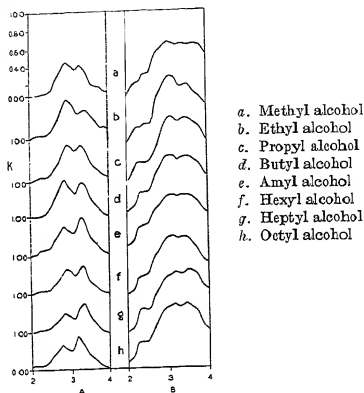


FIG. 10.6.—Absorption spectra of a portion of an homologous series of alcohols, (A) solution in CCl_4 , (B) liquid (Ellis [C48]).

1 to 20 μ on what we have termed the rotation-vibration spectra, more commonly known as the vibration spectra.

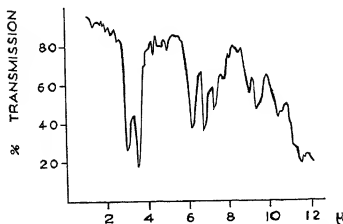


FIG. 10.7.—Absorption spectrum of *n*-butylamine (Bell [C4]).

By means of reasonably good resolution it has been possible to show, in the 1.76 μ band of hydrochloric acid (first harmonic of the 3.4 μ band),

a doublet structure indicating the relative amounts of Cl^{35} and Cl^{37} as isotopes in the HCl gas (Fig. 10.4) (C34). Since an electrical moment is required to show rotational structure it is possible to apply the study of band spectra to such compounds as carbon dioxide to determine the vibrational and angular conditions in the molecule. The vibration spectra can thus be applied to the coupling between ions or atoms as differentiated from electronic spectra, involving transitions of electrons.

In the field of liquids one finds a broadening of the absorption bands as was observed in the electronic spectra (visible and ultraviolet) (Figs. 10.5 and 10.6). From the data that have been obtained it has been possible to assign frequency or wavelength values to simple vibration linkages such as $\text{C}-\text{C}$, $\text{C}-\text{H}$, $\text{C}-\text{N}$, $\text{O}-\text{H}$, and to show that in homologous series intensity rather than frequency differences usually are found in the absorption bands (Fig. 10.6). A considerable amount of data has been collected by Coblenz (C129), Bell (C4), Ellis (C48) and others (Fig. 10.7) on the absorption spectra of organic and inorganic compounds, from which one can obtain characteristic spectral frequencies for many functional groups (Table 10.1). Since this field of spectral analysis was not contemplated as a portion of the radiant-energy effects to be discussed in this book those interested in the application and methods should consult the references given at the end of this chapter.

TABLE 10.1
FREQUENCY VALUES FOR INFRARED ABSORPTION BANDS DUE TO THE
INDICATED LINKAGES

Functional Group	Frequency ν'	Functional Group	Frequency ν'
$\equiv\text{C}-\text{H}$	2910 cm^{-1}	$-\text{S}-\text{H}$	2500
	990	$=\text{N}-\text{H}$	3300
$=\text{C}=\text{C}=\text{}$	1630	$\equiv\text{C}-\text{I}$	500
$-\text{C}\equiv\text{C}-$	2200	$\equiv\text{C}-\text{B}$	560
$=\text{C}=\text{O}$ (<i>Ketones</i>)	1722	$\equiv\text{C}-\text{Cl}$	650
$=\text{C}=\text{O}$ (<i>Acid</i>)	1660	$-\text{C}\equiv\text{N}$	2250
	1035		2150
	1034		1003
$-\text{O}-\text{H}$	3380	$-\text{NH}-\text{NH}-$	3000

RAMAN SPECTRA

Raman discovered in 1928 the phenomenon which is called the Raman effect (B24, B28) and which results from the scattering of light by a substance (usually a liquid, although solids and gases have been investigated). When a substance is illuminated by a monochromatic radiation, the molecules for the most part will transmit this radiation unabsorbed, i.e., if they absorb and give up the same light frequency they would become a point source and the light would appear to radiate from

the solution. To the degree that the molecules or particles in the solution absorb the energy and then re-emit it we speak of scattering of the light, and for colloidal particles the phenomenon is known as the Tyndall effect. Such an effect enables us to observe the location and motion of particles which exceed the normal limits of microscopic examination.

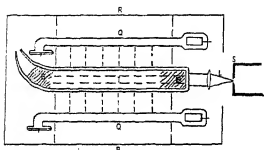


FIG. 10.8.—Apparatus for production of Raman spectra; tube for compound (*T*); mercury lamps (*Q*); reflecting box (*R*); spectrograph slit (*S*). The ends of the tube are usually blackened (*B*) to reduce direct illumination of the slit.

although the theory of formation permits negative values, and such values have been observed.

The frequency differences produced in the Raman spectrum are quite finite and are evidently due to quantized conditions. The usual differences are of the order of 15 to 250 f, which would correspond to the wavelength region of radiation from 20.0 to 1.2 μ or the region of vibra-

The important contribution that Raman made was the observation that this scattered light from a monochromatic illumination was not all of the same frequency as the incident beam. If ν_i represents the frequency of the incident radiation and ν_s the frequency of the scattered light, then we may represent the energy of these two rays as $h\nu_i$ and $h\nu_s$, and the energy difference between the two rays as $h(\nu_i - \nu_s)$, where $(\nu_i - \nu_s) = \Delta\nu$, or the Raman frequency. In general, $\Delta\nu$ is positive,

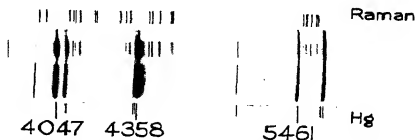


FIG. 10.9.—Raman spectrum of carbon tetrachloride (Jenkins).

tion-rotation band spectra. It can be shown that these observed frequency shifts are identical with the frequency intervals in the vibration band spectrum, and hence it is possible to observe these infrared values within the photographic radiation range. The usual method of observation is to illuminate a tube containing the liquid with a powerful discontinuous source such as a battery of mercury lamps and observe the scattered light from a flat end of the tube (Fig. 10.8).

Raman spectra determinations can be made with ease on the apparatus

available to the analyst who is equipped to do the usual types of absorption and emission determinations described in the previous chapters, and for this reason it may be worth while to indicate in more detail the type of results which can be obtained. The Raman spectra, like the vibration spectra in the infrared, indicates resonance relations between linkages, and, as with the vibration spectra, it is possible to assign certain frequency values to represent the resonance or vibration of certain link-



FIG. 10.10—Large aperture spectrograph for Raman spectra observation (Gaertner).

ages. In the simple inorganic compounds there is not much necessity to determine the presence or absence of certain linkages since the structure of most of the compounds is definitely known. In the field of organic chemistry, however, where a large number of isomeric compounds are possible it has been found useful to know the kind of linkages present in the compounds.

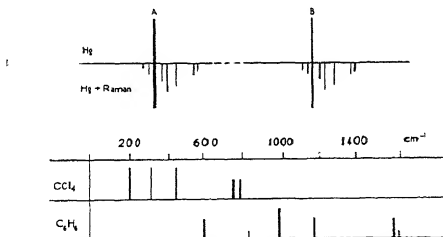


FIG. 10.11.—Raman spectrum analysis (length of line indicates intensity).

a. As observed in photograph (heavy lines A and B indicate exciting source).

b. Frequency analysis.

The characteristic frequency or displacement of the C—H linkage is about 90 f (2930 cm^{-1}) (equivalent to a position in the infrared of 3.41μ).

As can be seen from Table 10.2, the shift is not a constant one but is influenced by the other linkages in the molecule. The effect of these per-

TABLE 10.2
RAMAN SHIFTS FOR C—H LINKAGE

C—H aliphatic average.....	2918 cm ⁻¹	C—H primary aliphatic....	2862-2930
C—H aromatic average.....	3054	C—H secondary aliphatic..	2970

turbations, however, is not great enough to prevent the identification of the group or bond producing the shift. The figures in Table 10.3 repre-

TABLE 10.3
RAMAN SHIFTS FOR CHARACTERISTIC LINKAGES

Linkage	cm ⁻¹	Linkage	Cm ⁻¹
C—H aliphatic.....	2920-2970	S—H	2470
C—H aromatic.....	3054	C—S	645
C—C aliphatic.....	800-880	N=O nitrate	1640
C—C aromatic.....	1580-1608	nitrite.....	1640
C=C	1600-1650	nitro.....	1565
C≡C	2100-2250	C=N	1650
C—OH.....	820-880	C≡N	2150
C=O acid.....	1654	C—N nitro	910-930
ketone.....	1710	amine.....	880
aldehyde.....	1720	N—O	1000-1080
ester.....	1720	C—Cl	650-710
anhydride.....	1750	C—Br	570-600
O—H	3400	C—I	500-530

senting the frequency shifts are average values which are influenced by other linkages in the molecules. Raman band positions (intensities indicated by height) are usually published in the manner shown in Fig. 10.11b.

LITERATURE

General and Reference

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 "Infrared Analysis of Molecular Structure." F. I. G. Rawlins and A. M. Taylor (*A57*).
 "Der Smekal-Raman-Effect." K. W. F. Kohlrusch (*B24*).
 Bourgel and Piaux (*B2*), Lecomte (*B27*), Pringsheim (*B45*), Teller (*B51*).

CHAPTER XI

MEASUREMENT AND DESCRIPTION OF COLOR

DEFINITION OF COLOR

It is with some feeling of uncertainty and perplexity that one approaches the general subject of color and colorimetry. This feeling is caused largely by the inability of the physicist, the psychologist, the artist, and other interested persons to agree upon any common system of nomenclature for the physical description of color. Such expressions as color, brightness, hue, brilliance, intensity, purity, transmission, and level have no exact definition, and one finds some difficulty in the exact description of color terms. The sensitivity of the eye to various colors in the spectrum varies, as is indicated by the visibility curve of the eye (*C55*) (Fig. 11.1). The maximum sensitivity is at about $555\text{ m}\mu$, and the

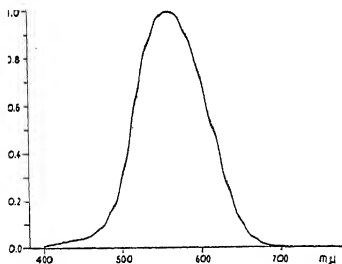


Fig. 11.1.—Visibility curve. Relative brightness of equal spectral energy (*C129*).

limits are about 400 and $750\text{ m}\mu$. This visual spectrum produces in the eye the stimulus of color sensation with spectral colors usually classified as follows:

Red.....	$750\text{--}620\text{ m}\mu$
Orange.....	$620\text{--}590\text{ m}\mu$
Yellow.....	$590\text{--}570\text{ m}\mu$
Green.....	$570\text{--}500\text{ m}\mu$
Blue.....	$500\text{--}450\text{ m}\mu$
Violet.....	$450\text{--}400\text{ m}\mu$

By purity of color one usually means the approach to monochromatic character in the color of the emitted, transmitted, or reflected light, or, in terms of a transmission spectrum, the narrowness of the transmission band. Color, as we generally recognize it, is the result of absorption, either by transmission of light through the sample or reflection from the sample. Reflection is a form of absorption in which certain portions of the spectrum are absorbed and the remainder are reflected. For example, a piece of colored Cellophane when held up to a light will transmit a certain portion of the spectrum and absorb the remainder. If the same piece is placed on a mirror surface and light is allowed to fall on it and to reflect back, one has a reflection spectrum which will correspond to the absorption spectrum.

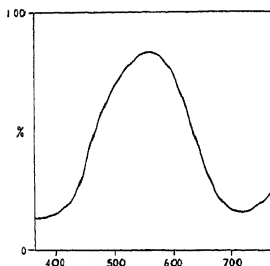


Fig. 11.2

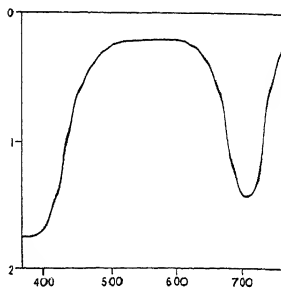


Fig. 11.3

FIG. 11.2.—Transmission curve of green sample.

FIG. 11.3.—Extinction curve (plotted downwards) of green sample used in Fig. 11.2.

It should be borne in mind that color, as one sees it with the eye, as a result of a colored filter or piece of paper, represents the light which is transmitted or reflected rather than that which is absorbed.

In our previous discussion we have dealt with light which was absorbed and with the measurement of absorption spectra, transmitted light being the complement of the absorbed light. Transmission (T) thus may be defined as equivalent to one minus Absorption (A), or

$$T = 1 - A$$

where $T = I/I_0$, or the portion of light transmitted, and $A = \frac{I_0 - I}{I_0}$, or the portion of light absorbed (these values $\times 100$ = the percentage of

COLOR PURITY

light transmitted or absorbed). In the "Handbook of Colorimetry" by Hardy (B17), use is made of the terms reflection factor and transmission factor; in the "Report on Spectrophotometry" of the Committee of the Optical Society of America (B14) the terms absorptivity and transmittancy are used for these values.

Blue color is produced by the absorption of wavelengths other than blue within the visible spectrum. To the chemist who is interested in the structure of the absorbing substance, this absorption region is of importance, and little attention is paid to the transmitted portion of the spectrum. From the standpoint of color production, however, it is the color transmitted which is of importance. The total portion of energy transmitted may be indicated as the area under the transmission curve (Fig. 11.2) as compared with the area above the curve. In the description of color and color values it thus appears that a more satisfactory indication can be made by the use of transmission or reflection in place of extinction (compare Figs. 11.2 and 11.3), although the same general characteristics are indicated in each curve. Transmission accents the portion of the curve at high percentage transmission and reduces the relative changes of the curve at low percentage transmission (see Fig. 8.43).

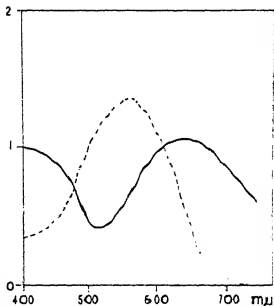


FIG. 11.4.—Green sample and its purple complement (dotted).

Color can be described by a curve, and this in turn by a mathematical formula. Such a formula would be too complicated to handle, and so an effort has been made to define color by means of an approximation into three factors—purity, brilliance, and dominant wavelength. Purity, as has been indicated, is a measure of the narrowness of the transmission band, where a single monochromatic line would indicate 100 per cent purity and a flat level transmission (typical of a gray) would represent 0 per cent purity. Brilliance, or brightness, as it is sometimes called, is a representation of the area included in the transmission portion as compared with the absorption portion, i.e., the total percentage of energy or light transmitted. The dominant wavelength is the wavelength of maximum transmission.

TRISTIMULUS VALUES

An analysis of color, as indicated above, would require a standard and uniform shape of all transmission bands, and, since these are irregular, it

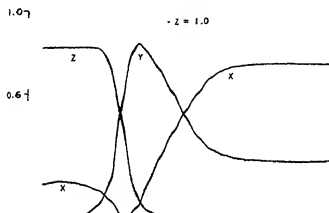


FIG. 11.5.—Trichromatic coefficients (proportion of each component in a given wavelength value).

becomes necessary to define the shape of the curve more exactly. This is done by dividing the visible spectrum into three portions and assigning to each portion a series of values so as to produce curves such as indi-

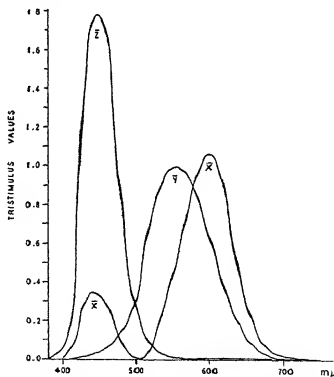


FIG. 11.6.—Distribution coefficients for equal energy (tristimulus values).

cated in Fig. 11.5 as \bar{x} , \bar{y} , and \bar{z} . By a series of calculations described by Hardy it is possible to assign to each unit millimicron a definite coefficient for \bar{x} , \bar{y} , and \bar{z} , and the integration of these values will yield a set

of three numbers, X , Y , and Z , representing the color, the brightness, and the purity. In Hardy's system the tristimulus values are arbitrarily chosen so that one of them has two transmission maxima, \bar{X} , at 440 and 610 $m\mu$. Other systems designed to indicate color characteristics in terms of a three-number or tristimulus system have been suggested, e.g., the Wright system which takes the wavelengths 650, 530, and 460 $m\mu$ as primary standards (*C122*). In the end, the attempts to define colors in terms of three, or even more, primaries become useless when such colors as neodymium pink, tomato red, potassium permanganate, cobalt blue, or chlorophyll green are to be described (Fig. 11.7). Although many colors, especially grays, flat colors, and off shades of white, can be adequately described by this means, it does not suffice for a description of pure chemical compounds for which the absorption, transmission, or reflection spectrum is essential to define the color. In mixtures of compounds where broad smooth curves are obtained, one can apply with sufficient accuracy the tristimulus methods of analysis. Hardy points out that "although the tristimulus values do not provide so much information as the spectrophotometric data, they can be derived from the spectrophotometric data by a straightforward computation procedure. They therefore provide a fundamental basis for a language of color" (*B17*).

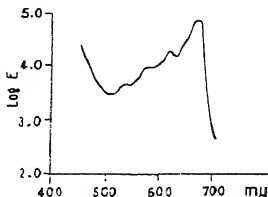


FIG. 11.7.—Chlorophyll green (chlorophyll $a + b$).

COLORIMETRIC APPLICATIONS

With the rapid increase in colorimetric methods of analysis a number of visual and photronic colorimeters have been devised for the measurement of transmission or reflection values of liquids, glasses, and colored papers. Most of these colorimeters are photronic in character, using a copper oxide cell, microammeter, and suitable light source (Figs. 11.8 and 11.9). A series of colored filters are supplied with these instruments so that light intensity may be determined for various wavelengths. The transmission curves are often given for these filters or can easily be determined (Fig. 11.10). As can be seen from the transmission curves, certain of the filters cut off the blue and transmit a portion of the red end of the spectrum; others are the reverse in that they cut off the red end and transmit the blue end, while the green has its highest transmission in the center. A dominant wavelength and a brilliance factor can be assigned to each of these filters, while those which overlap, such as the red

and orange, can be separated, i.e., by subtracting from the orange value the observed red value, inasmuch as the orange includes the red and orange spectral region. In a like manner, the yellow contains the yellow orange and red, so that subtraction of the observed orange from the observed yellow will give a true value for the spectral region bounded by the orange and yellow absorption curves. Essentially, this amounts to a series of five rather than three primary components. Additional com-

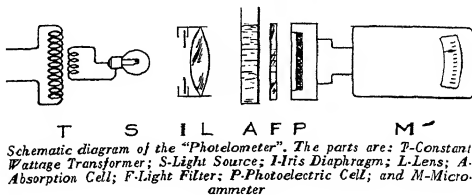


FIG. 11.8.—Diagram of a photonic colorimeter (Central Scientific Co.).

ponents could be added by corresponding cut-off systems in the blue and the use of purple filters with both a blue and red transmission.

In the usual colorimetric analysis it is desirable to determine the amount of colored material in the sample as compared with a standard value. For a blue solution the proper procedure is to use a red filter, since the solution, by virtue of its blue color, is known to transmit blue and absorb red. The amount of material present is measured, not by the

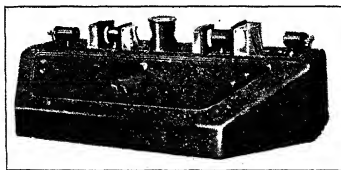


FIG. 11.9.—Photonic colorimeter (Kipp and Zonen).

amount of light the solution transmits, but by the amount it absorbs, and the most accurate measurements can be made by a spectrophotometric determination at the exact wavelength of its absorption band. A very good first approximation to the use of the absorption band wavelength is to utilize a filter which includes this wavelength and as little of the surrounding spectrum as possible. It is often difficult to convince the observer that one should use a blue filter for a red solution, but a brief

experiment will show that a red solution and a clear solution will look alike under a red filter whereas with a blue filter the clear solution will appear clear and blue and the red solution a black or very dark blue.

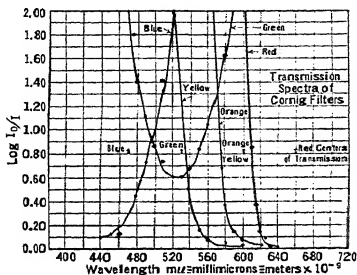


Fig. 11.10.—Transmission curves for color filters supplied with M. R. colorimeter (Brode [C19]).

In our discussion on the theory of the production of absorption spectra we pointed out that the introduction of additional chromophoric or

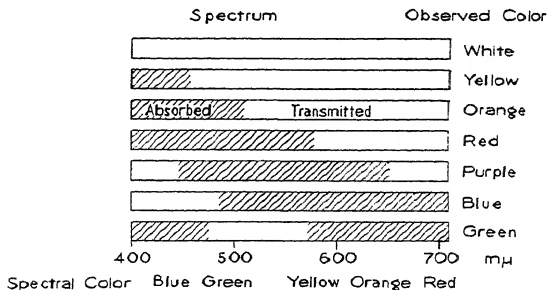


Fig. 11.11.—Absorption production of color.

weighting groups produced a hyperchromic and bathochromic effect, by which we meant that the absorption band was intensified and shifted to lower frequency values (i.e., towards the visible). As the absorption band is shifted towards the visible, it first approaches the violet end of the spectrum (Fig. 11.11) and in successive stages can be pushed across

the spectrum to reach ultimately the red side and even beyond, so that a second band will begin to appear from the blue side. The successive colors thus produced are as follows:

GREENISH

The color of a compound is thus said to be *deepened* if it goes from left to right in this order, i.e., from yellow to purple to green, and, though this is not the true spectral order nor these the true spectral colors, it repre-

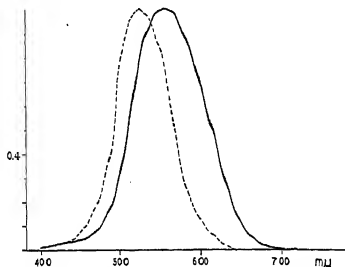


FIG. 11.12.—Twilight shift in relative visibility curve (change in chromatic response of the eye to equal intensity).

sents a very important series of color values. In these colors the yellow is not a spectral yellow but includes all the visible spectrum except the blue. In like manner the purple is a combination of two colors, blue and red, rather than a pure spectral color. It would seem, therefore, that color might be better defined on the basis of absorption rather than transmission effects.

It must also be recognized that the psychological definition of color involves other factors such as the response of the eye to environment, change of chromatic response with intensity (Fig. 11.12), and the frequency range of the observed radiant energy.

LITERATURE

"Handbook of Colorimetry." A. C. Hardy (*B17*).

"Measurement of Radiant Energy." W. E. Forsythe and others (*A15*).

CHAPTER XII

LABORATORY EXPERIMENTS

EXERCISE I

CALIBRATION OF MEDIUM-SIZE SPECTROGRAPH (WITH CORNU PRISM)

Optical Principle—Light Path. This experiment illustrates the use of the spectrograph in conjunction with a light source (an arc or spark) and condensing lens, L_3 (Fig. 12.1a). It is desirable, but not essential, that this light source and lens be on an optical bench so that adjustments may be

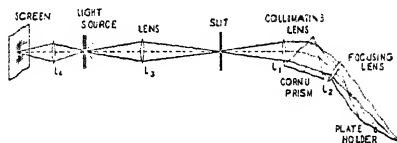


FIG. 12.1a.—Spectrograph with Cornu prism.

made without changing alignment of the optical path. This requires that the optical bench be parallel to the optical path of the spectrograph. A rapid method of determining the optical path is to place a strong single-filament light at K (Fig. 12.1a). (Note that K is the extreme right-hand end of the plate opening as one looks into the spectrograph through this opening.) This light path is the reverse of the normal path and makes possible a rapid adjustment of the apparatus. While this adjustment is being made, the slit of the spectrograph should be opened to about 0.1 to 0.2 mm.

Position of Source-Focusing Lens. The distance between the arc or spark and the spectrograph must be greater than four times the focal length of the lens, and it is preferable to use a greater distance and to place the lens at the focal position which produces the larger image, i.e., so that the lens is nearer to the light source than to the spectrograph slit. The choice of lens will depend to some extent on the size of the image to be projected. It is essential to have an image large enough to prevent the appearance of the electrode ends on the transmitting portion of the slit.

Position of Light Source. Once the optical path and focus have been established, it should not be necessary to alter the position of the lens, and any adjustment due to the failure of the image to center on the slit properly should be corrected by vertical or lateral movements of the arc or spark holder. If the light source wanders over the electrodes, it may be necessary to adjust the electrode positions continuously while the photograph is being made. Alignment may also be checked through the auxiliary image on the test screen. If the electrodes are of materials which produce nonconducting oxide layers, it will be necessary to start the arc by touching the electrodes with a carbon rod.

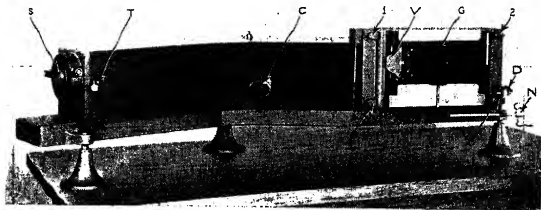


FIG. 12.1b.—Medium spectrograph (Bausch and Lomb). Focusing adjustment (*C*), slit (*S*), shutter (*T*), plate holder (*G*), dark slide (*V*), plate-holder screw-motion lever (*N*), scale lever (*D*), screw adjustment of plate-holder tilt (1,2,3,4).

Focus of Spectrograph Lens System. The spectrograph itself has many fine adjustments, but most of these are properly made and locked in position so that further adjustment should not be necessary. Such adjustments include the setting of the slit jaws to be parallel with each other, setting the slit so as to be parallel with the refracting edge of the prism, setting the prism at the angle of minimum deviation, and focusing the collimating lens. These pieces should be adjusted or altered with the greatest of care and only when absolutely necessary. For the most part any corrections which seem necessary may be made in the focusing of the lens system (the focusing lens L_2) and the tilt of the plate holder. A focusing screw is usually attached to the lens, L_2 or L_1 , by means of which the focal plane of the lens may be shifted.

In the absence of any known focus settings for the instrument, an approximate setting can be obtained by placing a sheet of ground glass in the plate holder at the right-hand end (longer wavelength end), and removing the back of the plate holder so as to observe the spectrum.

Slit. The width of the slit should be set at 0.02 to 0.03 mm (slit screws are usually graduated in 0.01 mm) and the height of the slit at about 4 mm by means of the wedge or Hartmann diaphragm.

Photographic Plate. Load the plate holder with a photographic plate (Eastman 33 is recommended since development can be easily observed with a No. 1 Wratten safelight). The plate should be numbered before leaving the dark room by writing with a pencil on the emulsion side at one end or a corner of the negative. This number should appear on the notebook or plate record sheet.

The observer should be careful in putting the negative into the plate holder so as to avoid fingerprints or abrasion marks on the emulsion side of the negative and should be certain that the emulsion side of the negative faces the safety dark slide of the plate holder. Putting the negative into the holder with the glass side facing the dark slide will result in a change of the focal plane by a distance equivalent to the thickness of the glass negative, thus throwing the spectrum out of focus, and, since glass is opaque in the ultraviolet beyond a wavelength of about 300 m μ , wavelengths shorter than this will not be transmitted to affect the photographic emulsion.

Experimental Procedure. A series of photographs are taken by moving the plate holder a definite distance at right angles to the spectrum, and at each setting a different focus value is used. The plate holder is usually moved by a gear or screw motion along a track with a graduated millimeter scale. The motion for each successive photograph should be about the same as the height of the slit (4 mm). The plate motion, like all other adjustments on the spectrograph (*except slit opening*), should be in a positive direction, i.e., from lower to higher positive values. If for any reason the motion exceeds the desired setting it is advisable to return to a position considerably behind the position desired and proceed in a positive direction to the point so as to avoid any instrumental back lash in the screw or rack motion. The series of photographs, as indicated in the accompanying sample data sheet, should start at a focus setting considerably below the approximate focus and should be increased in a positive direction until one has gone considerably beyond this approximate focus setting. For example, if the approximate focus is observed at a setting of +0.2 on the focus screw and it is apparent that settings of +1.0 and -1.0 are decidedly out of focus a series of photographs might be taken as indicated in the sample record sheet (Table 12.1).

Among the points to be observed are such routine procedures as:

1. Properly "facing" the photographic negative in the holder.
2. Opening of the dark slide of the plate holder *after* racking or sliding into position on the spectrograph.

TABLE 12.1
SPECTROGRAPHIC ANALYSIS

Plate No. ¹				Observer.....			
Instrument.....				Date.....			
Emulsion.....				Developer.....			
No.	Check ²	Plate Motion ³	Sample	Time	Source	Slit	Focus
1	✓	0 mm	Scale				
2	✓	4	Brass B-2	4 sec	Arc	0.02	-1.0
3	✓	8	Brass B-2	4 sec	Arc	0.02	-0.5
4	✓	12	Brass B-2	4 sec	Arc	0.02	-0.2
5	✓	16	Brass B-2	4 sec	Arc	0.02	0.0
6	✓	20	Brass B-2	4 sec	Arc	0.02	+0.1
7	✓	24	Brass B-2	4 sec	Arc	0.02	+0.2
8	✓	28	Brass B-2	4 sec	Arc	0.02	+0.3
9	✓	32	Brass B-2	4 sec	Arc	0.02	+0.4
10	✓	36	Brass B-2	4 sec	Arc	0.02	+0.6
11	✓	40	Brass B-2	4 sec	Arc	0.02	+1.0
12	✓	44	Scale				
13 ⁴	✓	50	Brass	6 sec	Arc	0.01	+0.2
14	✓	54	Brass	4 sec	Arc	0.02	+0.2
15	✓	58	Brass	2 sec	Arc	0.05	+0.2
16	✓	62	Brass	1 sec	Arc	0.10	+0.2
17	✓	66	Scale				

¹ The plate number should always be recorded on the data sheet or in the record notebook as well as on the negative.

² Check each exposure when completed.

³ All adjustments and settings involving a screw or rack motion and measured by a graduated scale should be made in a positive direction only. If the screw is graduated in both directions from a zero indication, one direction, preferably right, must be marked as positive, and settings made in a direction towards greater positive values.

⁴ Since the usual plate motion is about 80 mm (for a 4 by 10 inch plate) it would be of interest to test the effect of width of slit on the appearance of spectral lines. To do this the instrument should be set on its approximate focus and the indicated photographs taken on the bottom of this plate.

- Swinging the scale into position before turning on the scale lamp.
- Turning off the scale lamp after the scale exposure is made.
- Swinging the scale out of position after the scale exposure is made.
- Screwing or racking the plate holder to higher settings after each exposure and properly checking the observation record on the sheet.
- Opening the shutter before making exposures if the spectrograph is equipped with a shutter.
- Checking the slit and focus settings.
- Making the proper record on a data sheet or notebook of the nature of each sample observed.
- Observing the same precautions for the scale at the end of the plate as at the beginning.

11. Completely closing the dark slide before removing the plate holder from the spectrograph.

12. Being sure that the negative number agrees with the number on the data sheet.

Development of Plate. In a laboratory in which regular spectrographic analyses are made, standard developer solutions and a time-temperature control on the developing process will usually be provided. For instructional purposes and to avoid contamination from developers used by different workers where a large number of people must work with the equipment, it is suggested that each group or section of workers should prepare its own developer solutions. For this purpose the standard M-Q (elon-quinol) developing powder tubes are quite satisfactory. The solution is prepared by dissolving first the A powder and then the B powder in 250 ml of water at 70° F. A 250-ml graduated cylinder is convenient for

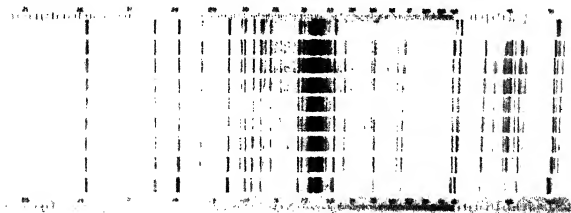


FIG. 12.2.—Focus negative (Exercise I).

the solution preparation, and if the carbonate powder (B) is added rapidly and shaken quickly and thoroughly it will not tend to form the less soluble hydrated form but will go directly into solution.

The number 33 plate should be developed about 1.5 to 2 minutes or until inspection from the back (glass) side with a No. 1 Wratten safelight shows the spectral image as having distinctly penetrated the emulsion. For more accurate work a time-temperature-developer control is essential to produce the desired gamma (see section on photography), but for focus calibration and qualitative analysis the above technique is quite satisfactory.

After development the plate is washed for about half a minute with water containing a small amount of acetic acid and then placed in the hypo (sodium thiosulfate) solution to clear. After the plate has been in the hypo for half a minute the white lights in the dark room may be turned on and the remainder of the procedure conducted in normal room lighting. The negative should stay in the hypo for about 10 minutes after

the last visual trace of silver halide (opaque light yellow color) has disappeared. It should then be washed for 15 to 30 minutes in running water at about 65 to 70° F. Before being placed in the drying rack the negative should be carefully washed with a wet hand, cotton swab, or viscose sponge to remove any scum or deposit which may form as a result of hard water or other adhering materials.

Examination of Negative—Report of Results. The dry negative should be carefully examined with either a projection apparatus or a reading magnifier (such as the Bausch and Lomb magnifier with a built-in scale). The report on the experiment should indicate the setting which produces the best focus in the middle of the spectrum or plate. In addition, the observer should examine the two ends of each spectrogram, and from the focus of the lines at the ends of the spectrograms he should indicate the most satisfactory focus settings for the long- and short-wavelength ends of his negative. If these latter values are not found in the same spectrogram or the same setting as the satisfactory center focus the observer should indicate the direction and amount of rotation that should be given to the plate to produce a more satisfactory focus adjustment.

Problem. The higher positive values of the focusing screw move the focusing lens nearer to the plate,¹ thus moving the focal plane away from the prism. If the spectrum is in focus at the low-wavelength (left) end at a setting of -1 , in focus at the center at $+1$, and in focus at the long-wavelength (right) end at $+3$, indicate the correct setting and the direction of rotation of the plate holder which should be made about its center (0 in Fig. 12.1a).

¹ Bausch and Lomb instrument.

EXERCISE 2

QUALITATIVE IDENTIFICATION OF ELEMENTS

This exercise is divided into two parts: (a) the identification of the lines of a known element, and (b) the determination of the wavelength values of the lines of certain unknown elements and the identity of elements which produce them.

Samples. It is suggested that a pure sample of copper be used for the first part, and a brass, aluminum alloy, or dye-cast alloy for the unknown. For the unknown one should avoid an alloy containing iron or other elements which produce a large number of lines.

Experimental Procedure. The V-wedge or Hartmann diaphragm in front of the slit should be set so as to give a spectrum about 4 or 5 mm wide, and the plate motion should be moved by this amount or the Hartmann wedge shifted so as to keep the scale and spectra in contact. Arc exposures should be made of the samples, using a current of about 4 amperes and a voltage drop across the electrodes of about 50 volts. (Table 12.2.)

TABLE 12.2
SPECTROGRAPHIC ANALYSIS

Plate No.		Analysis for.....			Observer.....		
Instrument.....		Copper—Brass.....			Date.....		
Emulsion			Developer.....		
No.	Check	Plate Motion	Sample	Time	Source	Slit	Focus
1		10 mm	Scale				
2		14	Copper (std)	5 sec	arc ¹	0.02 ²	+0.2
3		18	Brass C-3	5 sec			
4		22	Scale				
5	15 ²						

¹ On spectrographic data sheets it should be understood that, where there is no change in the method, slit width, focus, etc., on a plate, an entry at the top of the column is sufficient.

² The observer should either repeat these photographs on the remaining part of the negative or run another unknown in this space.

Development of Negative—Preparation of Chart. Develop the negative in the usual manner (see Exercise 1 and section on photography), being careful to wash the plate thoroughly after removing it from the fixing bath, and also to wash off with moistened cotton, viscose sponge, or with the hand any surface dirt or deposit prior to putting it into the drying rack. When the negative is dry put it into the enlarging machine (emulsion side down), and project the image so as to give a spectrum between 2400 and 5300 Å of about 28 to 30 inches. Such an enlargement will be about 3 to 3½ inches wide and can be made on three strips of 4 by 10

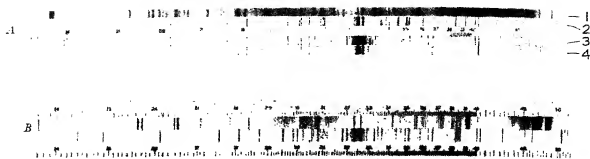


FIG. 12.3.—Sample negatives (A) aluminum alloy-copper, (B) spectrogram of aluminum alloy (1), aluminum bronze (2), copper (3), and brass (4). (See film in back pocket in this book, Sections A and B. [Film negatives are not included in special student edition.] N.

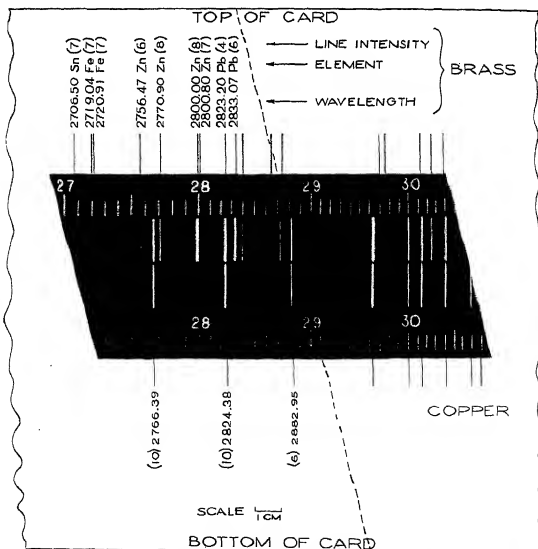


FIG. 12.4.—Enlarged section of mounted and partially identified spectra. P.

inch Eastman News Bromide or Agfa Brovira (contrast) paper.¹ Most enlarging machines will not project the entire 8- or 10-inch negative at one time but will require moving a negative of this size in the holder so as to produce three separate sections which may be combined to produce a complete enlargement of the negative (Fig. 12.5). The prints should be exposed to give a maximum gamma, and developed in M-Q or Agfa 125 developer. When dry the prints are to be trimmed and mounted on an 11 by 28 inch card with dry mounting tissue or rubber cement.

Identification of Standard (Copper)

Lines. Lines should be drawn on the card adjacent to each spectrum line, and the copper lines identified by reference to tables and by the photographed scale. For the identification of the copper lines it is suggested that one use the copper spectrum table in the "International Critical Tables," also in the "Handbook of Chemistry and Physics," or the copper table (page 380) in this book. Starting with the very intense copper pair of 3247 and 3273 Å, the remaining strong and then the weaker lines of copper can easily be identified, especially with the aid of the approximate wavelength values as given by the printed scale.

Identification of Unknown Lines. For the identification of lines other than copper, and in the unknown sample, one should use the table of persistent lines of the elements arranged by wavelengths, which is to be found in the same collection of spectrum tables

¹ See discussion in Chapter XIII, page 301, on the use of a special nonshrinking mappaper.

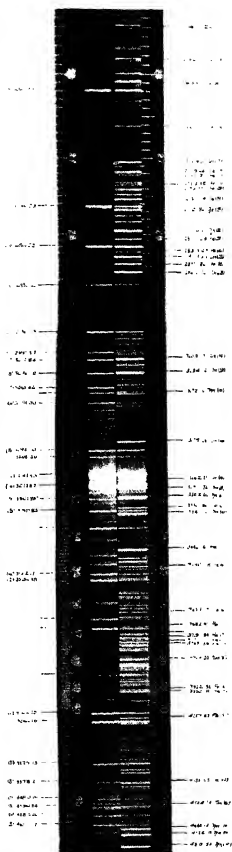


Fig. 12.5.—Report on Cu-Brass analysis. P.

(page 328) in this book. For example, if an unknown line of 2850A is present, it may be recorded as 2839 (Sn), 2843 (Cr), 2848 (Mo), 2849 (Cr), 2852 (Mg), 2854 (Pd), etc., depending on the accuracy of the photographed scale. In addition, the line may be a weaker line of some other element which is not given in these very abbreviated tables. For the preliminary survey it is best not to consult the very extensive tables such as Kayser's "Hauptlinien" or Harrison's 100,000-line table. In the above example, the persistent lines as arranged by elements should be consulted first; then the position of other lines of the possible elements should be noted and looked for in the photograph. If three or more lines agree, the presence of the element is practically certain. After identification of the element the wavelength tables for that particular element should be consulted, and the other strong lines of the element in the photograph identified.

An example of the method in which the data should be recorded is given in Fig. 12.4. The three strips should be mounted on the 11 by 28 inch card with dry mounting tissue or rubber cement, overlapping spectral regions being cut off so as to make a continuous strip, and, if the strip is longer than 28 inches, some of the short-wavelength end should be cut off to fit the card.

Reference Tables. For the solution of this exercise use the following tables (in this book) in the order indicated:

- (a) Copper spectrum. Table IV, p. 380.
- (b) Persistent lines by wavelength. Table I, p. 328.
- (c) Persistent lines by elements. Table II, p. 330.
- (d) Principal lines by elements. Table IV, p. 385.
- (e) Principal lines by wavelength. Table III, p. 332.

Film Spectrogram. In the negative reproductions in the Appendix (Section A) there are spectrograms of brass (4), copper (3), aluminum bronze (2), and aluminum alloy (1) unknowns which can be solved as additional unknowns or used as the unknown for this exercise in case the available spectrograph or samples are not satisfactory for this experiment (Fig. 12.34). It is suggested that the negative sheet be removed from the book and treated as an original negative in making the enlargements. It may be necessary to cut the negative to permit use in some enlarging machines, in which case one should avoid cutting through any of the spectrum photographs. (*Film spectrograms are not included in the special student edition.*)

EXERCISE 3

CALIBRATION AND ADJUSTMENT OF A LITROW SPECTROGRAPH

Optical Principle. The Littrow spectrograph (Fig. 12.6) embodies the same general optical principles as the Cornu prism type of spectrograph described in Exercise 1. The essential difference is that a single 30° prism is used rather than the two 30° prisms which make up the Cornu prism. The back or altitude face of the prism is coated with an aluminum or mercury amalgam so as to reflect the light back through the prism. The total light path thus is equivalent to a 60° prism, and any double refraction produced by the quartz as the incident beam passes through it

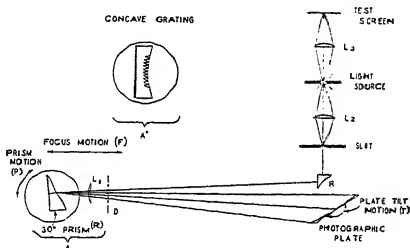


FIG. 12.6.—Littrow spectrograph.

is corrected in the reflected beam. The lens (L_1) also serves the double function as the collimating and focusing lens.

Some Littrow instruments are equipped with interchangeable sets of glass and quartz prisms and concave gratings. The most acceptable type of grating instrument for general analytical work is that in which a concave grating (A') takes the place of the lens (L_1) and prism (P) in the Littrow mounting. This concave grating mounting (see Fig. 3.12) is known as an Eagle mounting (A'). The procedures of adjustment and calibration for the grating and prism system are alike. Both types of instruments require the refracting axis, edge of the prism or the lines of the grating, to be parallel to the slit and perpendicular to the optical path of the spectrograph.

From a theoretical point of view the incident and dispersed beam should be centered in the same path; but this would be possible for one wavelength only, hence there is no serious objection to the spreading of the two beams so that the reflecting prism (R) of the incident beam lies just on the edge of the plate field. Placing this to one side avoids the obstruction of a portion of the photographed spectrum.

Slit Illumination. For purposes of obtaining uniform slit illumination

(see section on quantitative spectrographic analysis) it is sometimes advisable to place the condensing lens of the slit illumination system as close to the slit as possible and to place the light source so as to focus on the lens of the spectrograph. Such a modification of the conventional system of illumination is rather inefficient with regard to the dispersing system but permits the masking of the electrode ends of the light source (diaphragm [D], Fig. 12.6) and at the same time provides uniform illumination of the slit.

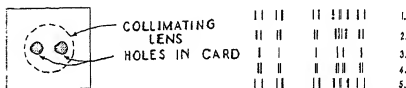


FIG. 12.7.—Effect of a two-hole diaphragm in focus adjustment.

The rather long path between the condensing lens and the spectrograph lens, as compared with the distance between the light source and the condensing lens, requires that the position of the light source be accurately determined and maintained in order that the image of the electrode ends may be properly masked (D) at the spectrograph lens (L_1), and the remainder of the arc fill as much of the spectrograph lens as is possible. To provide an accurate control of the position of the light source it is suggested that a supplementary lens (L_2) and a screen (S) be provided in the optical path. The optical path of the spectrograph can easily be established by setting the prism to a visual spectrum setting and placing a light at the position of the plate holder. The slit should be opened to about 1 mm and the location of the lens (L_2), light source (LS), auxiliary lens (L_1), and test screen (S) established.

Focusing. The focusing of a Littrow spectrograph involves three separate adjustments: (a) the focus setting of the lens, (b) the tilt of the prism, and (c) the tilt of the plate holder. The most sensitive of these adjustments is the tilt of the prism, so that for most adjustments this is set at approximately the correct setting as determined from known settings, or by observation with a ground glass in the visible portion of the spectrum, and the other two settings changed until adjustment is reached. By illumination of separate areas of the lens (L_1) with a two-hole diaphragm one can easily see a doubling effect when the instrument is out of focus (Fig. 12.7).

Usually each instrument of this Littrow type has a special table of settings calibrated for that instrument so that it will not be necessary as a rule to make the rough approximations as described above. The laboratory experiment involves the checking of one of the settings from

an accepted list for the instrument used. In this experiment a series of 10 photographs is to be made at varying focus settings, starting 4 units below the accepted value and changing the focus in unit increments for each photograph until a focus setting of 5 units above the indicated setting is reached.

Table of Settings. The following settings are given as an example of adjustments. These have been tested and found satisfactory for a Hilger Littrow Spectrograph (E 185):

TABLE 12.3

FOCUS SETTINGS FOR HILGER LITTROW SPECTROGRAPH (E 185)

Setting No.	Range Covered	Prism ¹	Focus ¹	Plate Tilt
1	2180-2455 A	64-18	126-10	64.2
2	2404-2794	65-15	141-04	64.9
3	2706-3286	66-12	157-00	65.9
4	3258-4448	67-09	174-00	67.2
5	3669-5324	67-17	182-18	67.6
6	4200-8000	68-02	189-04	68.5
7	2894-3690	67-00	164-10	66.3

¹It should be noted that focus and prism values on this instrument are operated by screw motions with graduated scales which are divided in to 20 parts per large scale division and not in the usual decimal or 10 parts.

This is an unusually large instrument having a focus of 3 meters as compared with a focus of approximately 1.75 meters for other large Littrows.

Automatic Instruments. Adam Hilger, Ltd., also manufactures an instrument (E 492) which is fully automatic, i.e., the three adjustments (prism, focus, and plate tilt settings) are made simultaneously by one control. This instrument has a focus of 1.7 meters.

The Bausch and Lomb Optical Company's large Littrow spectrograph is semiautomatic, in that coordination between focus and prism rotation is secured by means of a cam, which causes the prism to rotate as it is moved forward or backward in focusing. Eleven fine-pitch micrometer screws are inserted in this cam at suitable intervals, and each of these is accurately adjusted so that, when the screw carried on the arm which rotates the prism table bears on the end of a given screw, the portion of the spectrum is brought on the plate which is in focus with that position of the focusing carriage. The plate tilt is adjusted by a separate control. The focus of this instrument is approximately 1.8 meters.

The Hilger E 492, the Bausch and Lomb, and the Gaertner Littrow instruments have approximately the same focus, dispersion, and resolving power.

Although these instruments are fully or partly automatic the directions given above for making adjustments apply to them if any one of

the three settings becomes thrown out of adjustment and thus all three must be readjusted.

Experimental Procedure. Exposures should be made with a slit width of 0.02 to 0.03 mm, with an iron arc (4-ampere 50-volt drop) as a light source and exposing for 10 to 15 seconds. The same precautions and tech-



FIG. 12.8.—Focus negative (Exercise 3). *F* = focus adjustment, *P* = prism tilt, *T* = plate tilt. *N*.

nique are required as in the exposures described in Exercise 1. The negative should be developed as indicated in Exercise 1 and the section on photography (page 298).

Report. The negatives obtained should be examined as in Exercise 1. The report should confirm the setting or a suggestion made for its correction if the setting appears to be in error.

Problem. Plot the above Table 12.3 prism, focus, and tilt values against the range limitations. From these data determine approximate settings and upper range for a setting which yields a spectrum with its lower wavelength edge at 2600 Å.

EXERCISE 4

IDENTIFICATION OF A PORTION OF THE IRON SPECTRUM; PREPARATION OF A CHART FOR THE QUALITATIVE IDENTIFICATION OF AN UNKNOWN

Preparation of Spectrum Enlargement. A negative (Fig. 12.9) with a satisfactory iron spectrum, such as obtained in the final test run in Exercise 3, should be marked off into ten numbered spaces of 25 mm (1 inch) of the spectrum. Prepare enlargements of each section 10 times the original size. One section is to be assigned to each student, who will

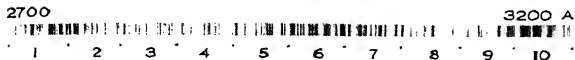


FIG. 12.9.—Iron spectrogram with indicated division assignments. N.

mount the photograph as indicated below and identify the iron lines in the 10-inch photographic strip. It is suggested that, for the enlargement of the small portion of this negative to 10 times its size, it will be found more satisfactory to use a miniature film enlarger such as the Magniphot-Zeiss, Omega, or the Leica apparatus. These enlargers are designed to cover a field of about 1 inch and give better definition in the final print.

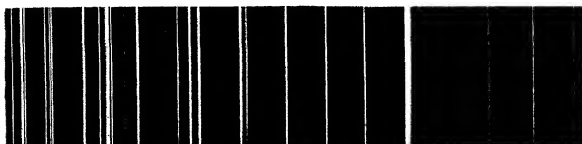


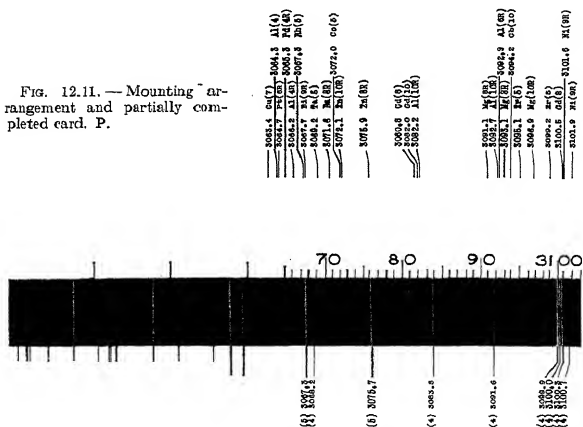
FIG. 12.10.—Enlarged section of Fig. 12.9. P.

Mounting of Enlargement. The final print should be at least 1 inch wide and is to be mounted in accordance with the arrangement shown in Fig. 12.11. The strip should be set so that its bottom edge is $1\frac{1}{2}$ inches from the bottom of the card. Above the strip and scale there should be a blank space upon which the spectra of unknowns may be projected. Above this space are to be indicated the principal lines of other elements which would appear in this region if the elements were present in the unknown. The number of lines indicated in this section will depend on the spectral region.

Identification of Iron Lines. In order to start in the identification of the spectrum, two iron lines should be identified by the instructor or from standard iron charts after the photographs have been mounted. The remaining iron lines should be identified from iron tables (page 387) as far as possible without reference to the available iron charts such as Hilger, Bardet, Crook, or the charts in this book (Plates II to XXXVI).

Wavelength Scale. The wavelength scale between the two spectra should be composed of unit lines not over $\frac{1}{8}$ inch high and numbers about $\frac{1}{8}$ inch high. The scale should be printed on the card after the iron lines have been identified, and if an instrument of high dispersion

FIG. 12.11. — Mounting arrangement and partially completed card. P.



place, the element symbol, and the indicated intensity on the 1 to 10 scale, i.e., 2519.2 Si (SR). So far as possible one should record all these identification lines in a single row on the card, but if there are too many in any particular portion of the card a second or even a third row may be required. The selection can be made by the use of intense lines (bold-face and ordinary type in Table III), and omitting the weak lines (italic type). It will be necessary to look up these lines in the tables of lines arranged by elements (Table IV) so as to obtain the intensity and first decimal angstrom value. (See Fig. 4.5 for examples of completed chart.)

If the class is sufficiently large a complete spectrum table may be prepared in addition to the students' obtaining some experience in the identification of spectrum lines. Individual workers or small groups will not find it of advantage to prepare more than one or two of these cards per person, and hence a reduced set has been included in this book to permit rapid identification of qualitative unknowns (Plates II to XXXVI). (See Exercise 5.)

Film Spectrogram. In order to provide suitable laboratory material for this and the following experiment (Exercise 5) on the identification of unknown elements in a steel sample, a negative print of an iron spectrum, 2 in (E) and 3 in (F), has been included at the end of this book. The print can be used for these two exercises if the laboratory is not equipped with a high-dispersion Littrow-type spectrograph. (*Film spectrograms are not included in the special student edition.*)

EXERCISE 5

QUALITATIVE IDENTIFICATION OF ELEMENTS PRESENT IN A STEEL SAMPLE

This exercise is designed to illustrate the use of photographic charts for the qualitative identification of elements and the use of the iron spectrum as a reference spectrum in place of a printed numerical scale.

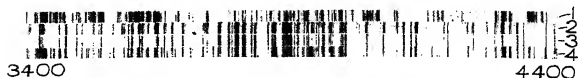


FIG. 12.12.—Unknown spectrogram. (1) Nonferrous alloy. (2) Steel. (3) Iron, (4) Steel. N. (Film strip *F* in back of book.)

Scale and Comparison Spectrum. Because of the variety of positions of adjustment that are possible with a spectrograph of the Littrow type,

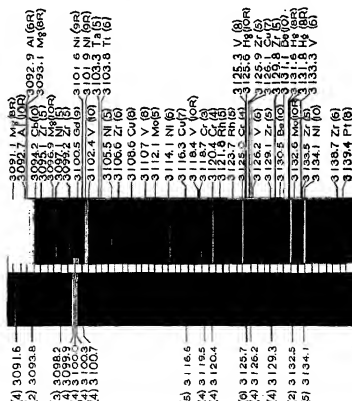


FIG. 12.13.—Use of cards for identification of elements (unknown spectrum enlarged to approximately the same scale as the card spectrum and enlargement strip (P) held in correct position). (Note: In the examination of nonferrous unknowns it is necessary to record on the original negative an iron spectrum in juxtaposition to the unknown and include this in the enlargement as shown.) This iron spectrum insures correct alignment of the strip on the card.

it is impractical to print a scale graduated in wavelength values on the photographic plate, as is done in the smaller Cornu-type spectrograph. In some of the more recent Littrow instruments, the design has been

altered so as to permit rapid adjustment and resetting to previously determined spectral ranges so that the use of a scale either in angstroms or in linear values is not an impossibility.

The iron spectrum has a very large number of lines, many of which have been determined with great accuracy so that some of them form part of our spectrum standards from which the wavelength values of other lines are determined. Because of the large number of iron lines the iron spectrum is essentially a graduated scale which can be printed onto the negative adjacent to the unknown spectrum, and the position or wavelength of the unknown line determined by its relative position between known iron lines. Although the iron spectrum is not so evenly graduated as a regular scale, it is a great deal more accurate than any scale which could be drawn and photographed on the negative.

Experimental Procedure—Preparation of Chart. For this experiment the spectrum of a steel sample is to be photographed and a 10 times enlargement prepared as in Exercise 4. For routine analysis it would not be necessary to enlarge this strip, but merely to project it on an identified iron-unknown card as obtained from Exercise 4, Plates II to XXXVI, or such charts as those given by Bardet or Crook, and to identify the unknown lines from the projection. If there are a large number of students in the group it is more satisfactory to use enlargements, making a strip about 3 inches wide and making 10 strips from a given negative, i.e., one print each from the 1-inch divisions of the negative. Each strip is then cut into three strips 1 inch wide, and each student identifies the elements other than iron present in a set of strips, using the cards prepared in Exercise 4 or Plates II to XXXVI for reference and identification (Fig. 12.12). The number of strips to be identified by each student will depend upon the amount and number of elements other than iron present in the sample. A sufficient number of strips should be assigned to each student so that there will be at least 50 lines (not 50 elements) other than iron to be identified.

Identification of Elements. In identifying the elements three steps are involved:

1. The wavelengths of all the unknown lines should be determined.
2. Tables of persistent lines, arranged according to wavelength, should be consulted in order to identify the elements present. If the persistent lines of a suspected element are not to be found in the spectral section under observation, the high-intensity lines of this element should be sought, as given in the tables of principal lines, since, as a result of the different methods of excitation, it is possible that the persistent lines of a singly ionized element may not be apparent, while those of the element of higher excitation state are apparent.

3. Check these possibilities by reference to the tables of persistent and principal lines arranged according to elements.

Report of Experimental Results. At least three lines of an element must be present for positive identification. The report should indicate the elements and wavelength values observed.

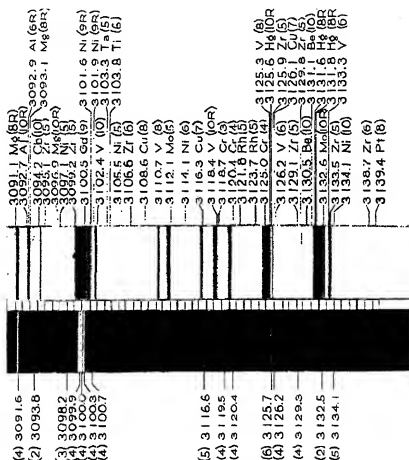


FIG. 12.14.—Use of cards for identification of elements. (Projection of unknown spectrogram with enlargement to the same scale as the card spectrum.) (Note: In this example the unknown is an iron-containing compound and hence no adjacent iron spectrum is required.)

Film Spectrogram. A film negative has been included at the back of this book showing a nonferrous alloy, No. 1 in (E) and (F) and two steel sample spectrograms, Nos. 3 and 4, taken on a Littrow spectrograph and suitable for this exercise if the observer's laboratory is not equipped with a high-dispersion spectrograph of the Littrow type. (*Film spectrograms are not included in the special student edition.*)

Problem. In Figs. 12.13 and 12.14 are given examples of the use of the comparison iron spectrum cards in the identification of unknown elements. Indicate the lines and elements present in each of the unknown spectrogram sections shown in these figures.

EXERCISES 6 AND 7

PREPARATION OF WORKING CURVES AND QUANTITATIVE DETERMINATION OF ELEMENTS BY THE LOGARITHMIC SECTOR METHOD (EXERCISE 6), AND BY THE PHOTOMETRIC METHOD (EXERCISE 7)

The principles involved in this determination are described in detail in the theoretical discussion on the influence of concentration on line intensities (page 77), and the description here will deal only with the application of these principles to the quantitative estimation of elements. It has been shown that for low concentrations of an element the intensity of its spectral lines bears a definite, although not linear, relation to the amount of element present. The measurement of this line intensity is further complicated by the fact that our usual method of recording a spectrum line is by the photographic process, which fails to record all light intensities in a linear density increase (see section on photography, page 295).

Since the two sections of this joint experiment deal with the measurement of line intensities by different methods, it is advisable to use the same set of knowns for both determinations in order that a comparison may be made of the two methods.

Preparation of Samples and Choice of Internal Standard. The preparation of a standard or working curve for use in either of these methods requires a series of samples containing varying known amounts of the "unknown" for which the analysis is to be made, in concentrations extending over the range expected in the samples which may be submitted for analysis. Each of these known "unknown" samples is to contain an added internal standard upon which reference intensity measurements can be made. The amount of this internal standard is to be constant in all samples in the series. Though not necessary in routine analysis it is suggested that two or three internal standards be used with each series in the experiment. The amount of internal standard to be added will depend, of course, on the internal standard lines that are to be used for comparison with the unknown lines and the relative intensities of these lines, i.e., for best results the unknown and standard lines should have about the same intensity in the middle of the range over which analysis is to be made. The photographic tables of Eder and Valenta (411) are valuable in indicating a choice of possible internal standards to be used with the unknown material. In the table of spectrum lines according to elements (Table IV, pages 365 to 434), lines which have been used by various observers for quantitative analysis, together with the lines that have been used as control or internal standard lines, have been indicated by S, B, L, etc. The conditions involved in the choice of an internal standard and unknown pair as indicated in the section on quantitative analysis require lines whose intensity or intensity ratio does not change

with excitation conditions (Fig. 5.2), whose intensity is sufficient for measurement in low concentration of the element, whose wavelength values are reasonably near together, and whose intensity is not appreciably influenced by extraneous elements present in the unknown sample.

It often happens that in commercial laboratories series of chemically analyzed samples containing varying amounts of a number of elements of known concentrations are available. Such series are especially desirable when one wishes to prepare a working curve of metallurgical samples. The choice of a sample depends largely on the nature of the products to which the method is to be applied. If the analysis is to be made of an alloy, then alloy samples should be prepared if possible; if the analysis is to be of a clay or refractory material, then a similar base composition should be chosen for the preparation of the standard samples. In the use of solution samples the standards can be easily prepared by dilution of a basic solution, care being taken that the anions present do not cause partial or complete precipitation of certain of the known or unknown elements. The solutions may be observed with a spark illumination as described by Twyman (Fig. 3.31) (*C113*). If an arc illumination is desirable the solutions may be evaporated in 1-inch cupped pieces of carbon electrodes (Fig. 3.21) and arched in the usual manner.

The preparation of standard samples for a clay or refractory series is somewhat more difficult but the exposure technique is simpler, and hence this is recommended as a laboratory experimental procedure to observe and compare methods. The same procedure has been found to work in the preparation of working curves of solutions. In a group of thirty or forty students the class is usually subdivided for convenience into five or six sections and each group prepares its own series of samples. Table 12.4 indicates possible combinations of elements for comparison studies and construction of working curves for quantitative analysis.

TABLE 12.4

Student Section No.	Internal Standard	Unknown
1	Cu, Pb	Ca, Sb, Bi
2	Mg, Zn	Cu, Hg, Pb
3	Cu, Hg	Mg, Zn, Sn
4	Mg, Pb	Ba, K, Cu, Hg
5	Zn, Sn	Pb, Cu, Mg
6	Mg, Bi	Zn, Cu, Ca

For each student section there are to be eight unknown samples, one standard (containing the internal standard only), and one blank sample (basic compound), as indicated in Table 12.5. In the method of preparation indicated in this table it will be noted that about 200 grams of No. 2 (basic compound + internal standard) are required and that in the end

one has available about 20 grams of each sample for analysis purposes. (If a solution method is used a corresponding number of milliliters will be required.) A satisfactory basic compound for this experiment is a mixture of 25 parts of silicic acid (anhydrous) and 100 parts of alumina (Al_2O_3) ground together in a ball mill to produce a fine free-flowing powder.

TABLE 12.5
PREPARATION OF SAMPLES

Sample No.	% Internal Standard	% Unknown	Method of Preparation
1 (Blank)	None	None	Basic Compound
2 (Standard)	1.0	None	1% of Each Internal Standard
3	1.0	0.001	23.3 g No. 2 + 10 g No. 4
4	1.0	0.00333	20 g No. 2 + 10 g No. 5
5	1.0	0.01	23.3 g No. 2 + 10 g No. 6
6	1.0	0.0333	20 g No. 2 + 10 g No. 7
7	1.0	0.1	23.3 g No. 2 + 10 g No. 8
8	1.0	0.333	20 g No. 2 + 10 g No. 9
9	1.0	1.0	23.3 g No. 2 + 10 g No. 10
10	1.0	3.333	3.3% of Each Unknown in No. 2

NOTE: Concentration of cations as given in percentages applies to the free element. In the preparation of samples 2 and 10 allowance must be made for anions such as the hydroxide or carbonate in determining the percentage of elements introduced.

In the preparation of some of these standard and unknown mixtures, solutions have been made of the metal ions and added to the clay together with sufficient water to form a mush; the mixture is dried in an evaporating dish on a steam plate with constant stirring and then ground in a mortar or ball mill to insure uniform distribution of the metal ions.

To shorten this preparation a modification has been tried, with reasonable success, in the grinding of the metal salts (preferably as the carbonates) with a small amount of the silica-alumina mixture (sample 1) and then grinding this with the remainder of the mixture required for the sample. The final 30 grams of the mixture is to be sampled by the "quartering process" used in analytical methods, and 10 grams of this is to be set aside for the preparation of the next mixture.

Experimental Procedure—Slit Illumination. In making photographs with the logarithmic sector a cupped electrode is to be used, and 10 exposures of 6 to 10 seconds each are made, refilling the electrode each time, thus making an exposure of 1 to 2 minutes for each sample. The first series of photographic exposures are to be made with a logarithmic sector in accordance with the method of Scheibe (459). This method requires that the sector be placed as near the slit as possible and that the slit be illuminated as uniformly as possible. For this uniform illumi-

nation one can best use a long-focus lens immediately in front of the sector (Fig. 12.15). This long-focus lens should bring the arc or spark to a focus on the collimating lens of the spectrograph, where a suitable diaphragm can be placed so as to cut out unwanted electrode portions of the arc or spark. If the light source is located at a distance from the lens, sector, and slit of about 30 to 50 cm and the distance from the slit to the collimating lens is this distance or greater, it is obvious that the position of the arc or spark must be carefully set and watched on the test screen during the exposure so as to be sure that the diaphragm in front of the collimating lens in the spectrograph is properly filled. If there is some uncertainty about the filling of this diaphragm and the spectrograph is easily opened for inspection it is worth while to open the slit to about 1 mm, illuminate the slit with the light source, and examine the image of the source on a white card placed in front of the collimating

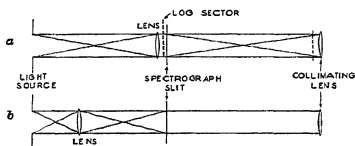


Fig. 12.15.—Position of slit illuminating lens. *a.* Slit wedge or logarithmic sector method. *b.* Normal use.

lens. One should, of course, be careful to close the spectrograph and reduce the width of the slit before opening the plate holder and proceeding with the observations.

Logarithmic Sector Exposures. It is essential in the use of a logarithmic sector (Fig. 5.4) that the cutting or straight edge of the sector be parallel with the slit at the moment at which it crosses the slit. The sector can be driven by a small synchronous motor such as the motor of an electric clock. In the use of the sector method it is usually necessary to remove the Hartmann or wedge diaphragm in front of the slit. In order to photograph the normal spectrum of iron as a comparison, on the lower edge of a logarithmic sector photograph, it is necessary to stop the sector, move the plate holder about 2 mm upwards (assuming that the sector is set so that its center of rotation is below the slit), and set the sector so that it makes an angle of about 90° to 180° with the slit (Fig. 12.16). This will produce a narrow spectrogram of about 2 mm below and in contact with the logarithmic sector spectrogram.

Since the logarithmic sector method uses the full slit aperture, the

LOGARITHMIC SECTOR METHOD

spacing between photographs will have to be 15 mm. To be sure of the purity of the electrode a photograph should first be made with the carbon electrode; then a photograph should be made of the silica-alumina mixture to determine what elements may be present in this mixture.

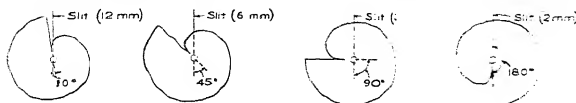


FIG. 12.16.—Slit and sector positions for stopped sector photograph (height of slit and spectrogram indicated in millimeters, based on a 15-mm maximum slit length).

The third photograph is to be a standard, i.e., the silica-alumina mixture plus the internal standard but without any of the unknown elements. After this the mixtures containing the "unknown" should be exposed, starting with the mixture containing the smallest amount and proceed-

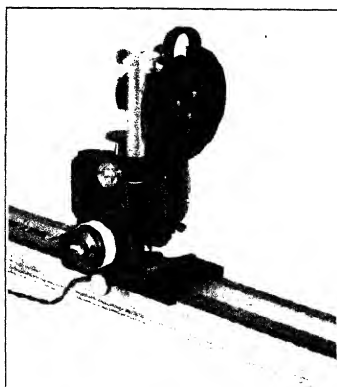


FIG. 12.17.—Logarithmic sector (Hilger).

ing to samples with higher concentrations of the unknown. By following this order of exposures it is not necessary to use new carbons for each exposure, although this would be done, of course, if one were working with substances of unknown concentration or preparing a working curve for exact quantitative analysis.

The carbon blank on the first negative should be taken at 0 mm on the plate position scale, the silica-alumina at 10 mm, and the remaining four exposures on this negative at 15-mm intervals. The sector should now be stopped and set at 90° to the slit (see Fig. 12.16). The plate holder should be moved to 72 and a 10-second iron spectrum taken.

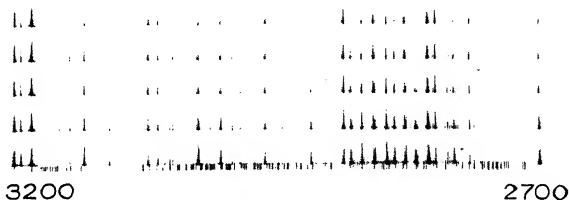


FIG. 12.18.—Negative 1 (Exercise 6-7).

The second negative will start with sample 6 and continue at 15-mm intervals to sample 10. The revolving logarithmic sector is again to be stopped and this time set to an angle of 45°, the plate holder advanced 5 mm from the previous photograph, and another 10-second iron spectrum taken. Slit width on both negatives should be 0.03 to 0.05 mm.



FIG. 12.19.—
Step-density
wedge (A).
Log-density
wedge (B).

Photometric Exposures. Continuing on the same negative, the photometric-method exposures may be recorded by making 6 exposures of about 6 seconds each with the electrode refilled before each exposure. For these photographs the sector should be stopped and set at about 45° and the plate holder moved 5 mm after each sample photograph. Starting with new carbon electrodes, the silica-alumina mixture, the blank with the internal standard, and the samples in the order of increasing concentration are to be photographed. After the last sample an iron spectrum should be taken, making 12 photographs in all.

Application of Density Pattern. Before these plates are developed they should be calibrated by having a density negative can be obtained from the Eastman Kodak Company). This wedge can be placed on the top of a printing box so that the low wavelength edge of the plate can be exposed. The time of flashing or exposing the density pattern should be such as to yield a gradation from opaque to transparent in the range of the wedge, after the nega-

tive has been developed. A more satisfactory and accurate method of plate calibration can be obtained through the use of a step wedge, or step sector in front of the slit, or a step slit (C44). By this method

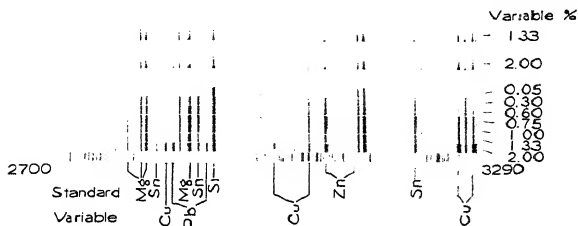


FIG. 12.20.—Negative 2 (Exercise 6-7).

a density pattern can be obtained for the negative at the same, or approximately the same, wavelength as that at which the analysis observations are to be made.

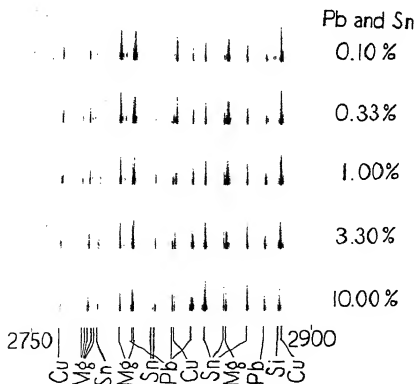


FIG. 12.21.—Enlarged section of Fig. 12.18.

Number of Negatives. The above series of photographs if made on a Littrow instrument should be made first at the setting of the spectrograph which includes the 3000-4000 Å region, and then repeated at the

setting which includes the 2500-3000 Å region. In all, four plates are to be prepared for this exercise.

Measurement of Line Intensity—Logarithmic Sector Method. Each student will be assigned one unknown element to be compared with one of

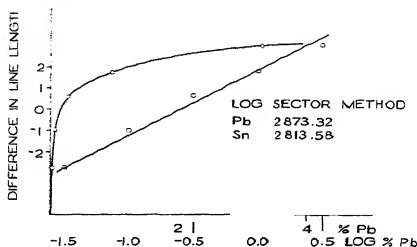


FIG. 12.22.—Logarithmic sector working curve.

the internal standards. It may be necessary to use several lines of either the known or internal standard before a satisfactory series can be located. The choice of line pairs has been discussed in an earlier chapter.

The lines by the logarithmic sector method (Fig. 12.21) are to be

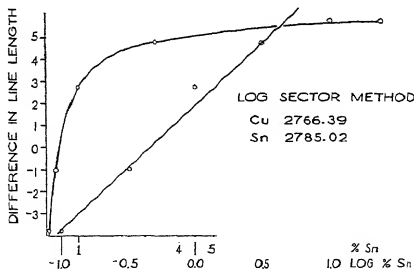


FIG. 12.23.—Logarithmic sector working curve.

measured to the nearest 0.1 mm by a graduated eyepiece. The measurement to be made is the length of the line from its end to the dark strip caused by the outer edge of the sector. A record (Table 12.6) should be made of the observed line lengths, and the difference between the lengths of the known and standard plotted (Figs. 12.22 and 12.23) against

DENSITOMETER METHOD

the concentration in percentage and against the concentration in log percentage. In the latter case a straight line should be obtained, at least over the effective portion of the concentration range.

Measurement of Line Intensity—Photometric Method. The series of spectrograms taken with the stationary sector (45° angle) so as to yield a line height of about 4 mm are to be measured by means of a densitometer. Any one of the available commercial instruments will prove quite satisfactory for this experiment, or one may construct his own instrument through the use of a projection system such as is available in a lantern-slide projector. The spectrum image is projected on a screen in which has been placed a slit with a photocell backing it (Fig. 12.24). The current from the photocell (415) can be measured by a galvanometer or sensitive microammeter, thus providing a measure of the line density. It is desirable to use a mechanical drive on the plate motion and to observe the maximum swing of the galvanometer as the spectrum line

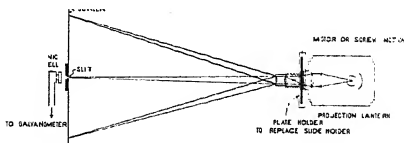


FIG. 12.24.—Spectrum plate densitometer.

passes in front of the slit; this is not necessary, however, and accurate results can be obtained from careful setting of the spectrum line in front of the slit by manual operation.

The observer should record the density (Table 12.6) of the unknown and internal standard lines in each of the spectrograms as indicated by the galvanometer readings. The observer should also record the galvanometer readings for a clear portion of the plate, the zero light intensity reading with the photronic cell covered, and the density values of the plate calibration wedge. The difference in density values of standard and unknown lines should be plotted against the concentration and log concentration of the unknown line (Fig. 5.15a). Since over a considerable portion of the plate density there is a linear relation between the density and the logarithm of the exposure or the logarithm of the intensity, this density difference should be equivalent to the difference in line length obtained by the logarithmic sector method.

Application of Plate-Density Calibration. To confirm this linear relation and supply any necessary correction to deviations from it, the galvanom-

TABLE 12.6

(FORM OF REPORT OF DATA IN EXERCISES 6 AND 7)

Spectrographic Laboratory

REPORT ON WORKING CURVE DATA

Observer.....	QUANTITATIVE	Plate No.
Date.....	SPECTROGRAPHIC	Method and Settings.....
Internal Standard <i>Pb</i> 2833.07	ANALYSIS	Base Material— $Al_2O_3 = 20\%$
Unknown <i>Bi</i> 3067.73		$H_2SiO_3 = 80\%$

No.	Concentrations			LOG SECTOR METHOD			DENSITOMETER METHOD					Ratio (I_{Bi}/I_{Pb})
	$Pb\%$	$Bi\%$	$Log Bi$	Length of Lines		Ratio	Deflection		Clear Deflection = 22.2			
				Bi 3067.73	Pb 2833.07	$Bi-Pb$	Bi 3067.73	Pb 2833.07	$22.2-Bi$ I_{Bi}	$22.2-Pb$ I_{Pb}		
1	22.3	
2	1.00	7.0	...	22.2	18.1	...	4.1	...	
3	1.00	0.001	-3.000	5.2	7.2	-2.0	21.8	18.0	0.4	4.2	0.095	
4	1.00	0.003	-2.477	6.3	7.2	-0.9	21.5	18.1	0.7	4.1	0.171	
5	1.00	0.010	-2.000	7.2	6.8	0.4	21.2	18.1	1.0	4.1	0.244	
6	1.00	0.033	-1.477	9.3	7.3	1.5	20.5	18.2	1.7	4.0	0.425	
7	1.00	0.106	-1.000	9.2	6.3	1.9	19.4	18.1	2.3	4.1	0.883	
8	1.00	0.330	-0.477	10.6	7.3	2.8	18.6	18.1	3.6	4.1	0.878	
9	1.00	1.000	0.000	11.2	8.1	3.1	17.9	18.0	4.3	4.2	1.025	
10	1.00	3.333	0.523	11.7	6.9	4.8	17.7	18.1	4.5	4.1	1.098	

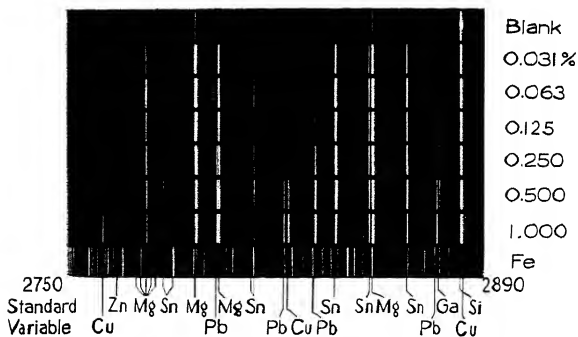


FIG. 12.25.—Enlarged section of densitometer negative. P.

eter values for the calibration densities should be plotted against a unit linear scale since the densities of the wedge steps bear unit log relations (Fig. 5.11b). The slope of the linear portion of the curve will represent the plate gamma, and corrections which are necessary to apply to the spectrum line intensities can be easily estimated. For example, if D_1 repre-

sents the density (galvanometer) value of a given standard line then the necessary correction which must be added to the reading is represented by d_1 . If D_2 represents the density of an unknown line then d_2 will represent the correction necessary to add to this value.

The density differences may thus be given approximately as $D_1 - D_2$ or more accurately as $(D_1 + d_1) - (D_2 + d_2)$. If D_1 and D_2 are nearly equal, then any correction which might be necessary would drop out in the calculation of relative intensity.

Report on Exercise 6. The report to be handed in for Exercise 6 (logarithmic sector method) should include: (1) a data sheet indicating the composition of the samples and observed line lengths and differences (see Table 12.6); (2) a curve indicating the relation between line length difference (relative intensity) and percentage composition; and (3) a similar curve indicating log percentage composition.

Report on Exercise 7. In the report which is to be handed in for Exercise 7 (the photometer method) there should be: (1) a data sheet indicating the composition of the samples and galvanometer readings for the samples and density pattern (see Table 12.6); (2) a $d \log I$ curve for the photographic plate, based on the density pattern; (3) a curve of the unknown-standard intensity (galvanometer differences plotted against percentage composition), and a correction curve based on the log density pattern; and (4) a curve of the log percentage composition-line density difference.

Film Spectrogram and Sample Data Sheet. If a logarithmic sector or a densitometer is not available, the essential figures for the experiment can be obtained from the sample data sheet (Table 12.1). In addition, the sample negative (Sections C and D) at the back of the book can be measured on a densitometer for the photronic cell method or with a measuring eyepiece for the logarithmic sector lines. In the absence of a measuring eyepiece the logarithmic sector portion can be enlarged and measured directly with a millimeter ruler. It is suggested that the following logarithmic sector pairs be identified, measured, and the differences plotted: Pb 2873/Mg 2781; Sn 2785/Cu 2766; and Sn 2913/Mg 2776.

Remarks. A convenient method of constructing a logarithmic sector is to draw on a piece of polar coordinate paper an accurate circular logarithm curve. A thin aluminum disk of the proper size is cut and drilled to the exact size of hole required to fit on the bearing shaft, which may be attached to the spectrograph. The disk is cut to approximately the same relative size and curvature as the drawing would indicate, although the disk will be about 1/10 the diameter. The disk is then placed on a glass plate in the holder of the enlarging machine, and the enlarging machine is focused to give almost the same degree of enlargement as the

polar coordinate drawing, centering the hole in the disk on the center of the polar coordinate sheet. One can tell from this enlargement the exact places on the disk where it is necessary to cut or file and the amount of such reduction required. The process of cutting and smoothing down must be continued until a perfect miniature reproduction of the paper curve is produced in the sector.

The calibration of a plate by means of the density wedge is made with a white light source. To be more accurate and to correct for certain possible errors in variation of plate emulsion sensitivity at various wavelength values, one should expose the calibration wedge with light of the wavelength at which the spectrum line is to be measured. This can be accomplished in part by means of a step slit such as Hansen (C58) and Duffendack (C44) have described, or by means of a step sector or step wedge placed in front of the ordinary slit. Lines adjacent to the spectrum lines under investigation can thus be measured to obtain the $d/\log I$ curve for the particular wavelength portion of the plate.

The pairs of spectrum lines used in the logarithmic sector method should be used in the photometric method, so as to provide a comparison of the two methods.

Problems. 1. Plot the logarithmic sector and the densitometric working curves for which the data are supplied in Table 12.6.

2. Plot the logarithmic sector and the densitometric working curves for which the data are supplied in Table 5.4.

3. Identify the 2873 Pb line and the 2781 Mg line in Fig. 12.21. Measure the length of these lines, and plot the working curve.

4. Identify the 2913 Sn line and the 2776 Mg line in Fig. 12.21. Measure the length of these lines, and plot the working curve.

EXERCISES

VISUAL ABSORPTION SPECTRA DETERMINATION OF GLASS AND SOLUTION SAMPLES

The object of this experiment is to determine the visual absorption spectra of certain colored samples. These determinations may be made on a visual spectrophotometer such as the Bausch and Lomb, Hilger-Nutting, Keuffel and Esser, König-Martens, etc. The Bausch and Lomb apparatus (Fig. 12.26) is equipped with a colorimeter type of cell holder (Fig. 8.19) which permits the measurement of the transmission of liquids of any desired thickness up to 6 cm. The instrument is designed so that the colored sample may be placed in front of either of the beams, but, in order to get positive readings on the observation scale, the colored samples should be placed in the right-hand beam.

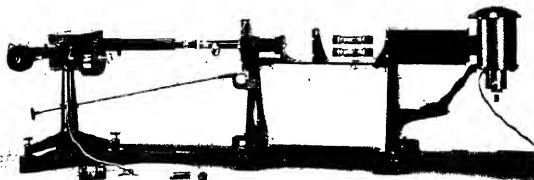


FIG. 12.26.—Spectrophotometer (Bausch and Lomb).
(See Fig. 8.19 for diagram.)

Determination of Match Point. No adjustment should be necessary, but it is advisable to observe the spectrum with both beams clear and to check whether extinction values remain zero over the spectral range. Two observations for each point to be plotted are made, i.e., one must observe the wavelength value and the extinction value. The match is observed in the eyepiece as a column of light, differing in color in accordance with the wavelength which is being observed, and divided across the center into upper and lower segments. A change of the extinction will, of course, alter the relative intensities of the two halves (Fig. 12.27). The width of the column or slit of light can usually be adjusted, and it should be set to as narrow a column as can be conveniently observed. The eyepiece itself can be focused by the focusing screw which is on the tube leading to the prism unit. In using the Bausch and Lomb instrument, care should be taken not to disturb the small screw by the eyepiece. This is *not* a focusing screw but determines the wavelength calibration of the instrument.

Photometer Scale. On the Hilger instrument the graduated photometer disk is divided in densities and degrees, the König-Martens and Gaertner instruments are graduated in a similar manner, and the Keuffel and Esser instrument is graduated in percentage of light transmitted. The Bausch and Lomb instrument has the photometer scale divided into three parts: one part, involving an angular swing of 180° , is graduated in degrees; the remaining two parts of 90° each are graduated (a) in percentage

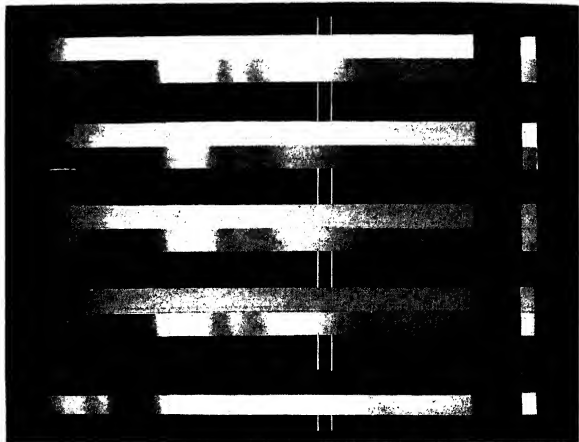


FIG. 12.27.—Match point and slit opening; strips indicate appearance of spectra at different extinction settings of comparison beam, with wide (left) and narrow (right) ocular slit.

transmitted, and (b) in the negative logarithm of the percentage transmitted, or, as commonly known, the extinction coefficient. (See Table IX for interconversion of these units.) In making observations, extreme care should be taken that the readings are made on the same scale, and not part on one and part on another, since the match points are observable on any of the scales. From a point of efficiency the best extinction values are observable from 0.5 to 1.8, and, if a solution is being used, the cell thickness should be altered to provide extinction values within these ranges.

Method of Observation. Data obtained for the test samples should be recorded on the data sheets and graph paper provided for this purpose (Figs. 12.28 and 12.29). It is advisable to make at least two readings per setting, and to make these rapidly (one or two seconds for each reading) rather than spending considerable time in trying to arrive at a satisfactory match point. If, with the slit of the eyepiece open, there appears to be no component structure in the observed sample, the readings should be made every 10 $m\mu$; but if there is a component structure such as is observable in a neodymium glass the readings should be made at least every 5 $m\mu$. Observations should not be attempted beyond 450 $m\mu$ in the

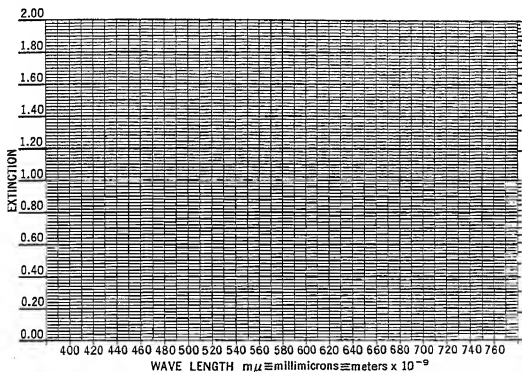


FIG. 12.28.—Form for graphical recording of spectrophotometric data.

blue or 720 $m\mu$ in the red. In the determination of absorption spectrum curves by a spectrophotometer it is suggested that the wavelength drum be set at definite values as indicated (Fig. 12.29) and the extinction adjusted to a match point, except for very sharp bands when it may become desirable to set the extinction to definite values, say every 0.1 or 0.05 E , and change the wavelength to obtain a match point.

The dispersion drum of the spectrometer can be obtained with frequency rather than wavelength graduations, should the operator desire to record his data principally in frequency values. If a record sheet similar to the sample (Fig. 12.29) is used it will be noted that frequency values (in fresnel units) are given in italic type in parentheses below the wavelength values, so that curves may be plotted directly from the data

FIG. 12.29

SPECTROGRAPHIC LABORATORY
VISUAL SPECTROPHOTOMETRIC ANALYSIS

No.

Sample (1) Conc. Sol. No. Observer.....
 (2) Conc. Sol. No. Date.....
 Solvent (1) (2) (UV. Plate No.)

	(1)		(2)			(1)		(2)	
	Cell	cm	Cell	cm		Cell	cm	Cell	cm
	Extinction	Av.	Extinction	Av.		Extinction	Av.	Extinction	Av.
440					590				
(682)	_____	—	_____	—	(609)				
450					600				
(687)	_____	—	_____	—	(600)	_____	—	_____	—
460					610				
(682)	_____	—	_____	—	(492)	_____	—	_____	—
470					620				
(638)	_____	—	_____	—	(484)	_____	—	_____	—
480					630				
(620)	_____	—	_____	—	(476)	_____	—	_____	—
490					640				
(612)	_____	—	_____	—	(469)	_____	—	_____	—
500					650				
(600)	_____	—	_____	—	(462)	_____	—	_____	—
510					660				
(588)	_____	—	_____	—	(455)	_____	—	_____	—
520					670				
(577)	_____	—	_____	—	(448)	_____	—	_____	—
530					680				
(566)	_____	—	_____	—	(441)	_____	—	_____	—
540					690				
(556)	_____	—	_____	—	(435)	_____	—	_____	—
550					700				
(546)	_____	—	_____	—	(429)	_____	—	_____	—
560					710				
(536)	_____	—	_____	—	(423)	_____	—	_____	—
570					720				
(526)	_____	—	_____	—	(417)	_____	—	_____	—
580					730				
(517)	_____	—	_____	—	(411)	_____	—	_____	—

sheet in either abscissa. It is highly desirable to plot the absorption spectrum curve while the sample is in the instrument and to examine the curve for apparent irregularities. These irregular points on the curve should be rechecked on the instrument to determine whether an error in reading has been made or whether the curve actually has an irregular shape.

Experimental Procedure. In this exercise the following observations, or such portions as the instructor may indicate, should be made.

1. Absorption spectra of cobalt, nickel, or other simple colored glass. (See Fig. 11.10.)

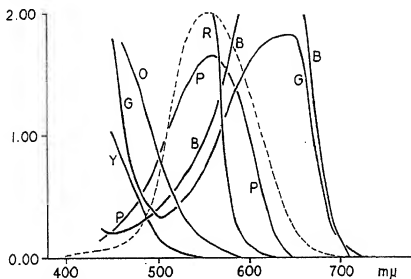


FIG. 12.30.—Absorption spectra curves of colored Cellophane films. (See Figs. 12.42 and 12.43.) Yellow (Y), orange (O), red (R), green (G), blue (B), purple (P). (See Cellophane inserts in back of this book.) (Dotted curve indicates relative visibility.)

2. Absorption spectrum of neodymium glass.
 3. Absorption spectrum of a dye solution (crystal violet).
 4. Absorption spectrum of a potassium permanganate solution. If the use of the apparatus is limited, it is suggested that samples 2 and 3 be selected. The colored solutions should be adjusted in concentration so as to give a maximum extinction value of about 2.0 E for the cell thickness used.
- Report.* The report should include data sheets and curves (in λ and E values) for the test samples.

Problem 1. Plot the curve of the data on sample 2 in the sample data sheet (Fig. 12.32):

- (a) on a λ (mμ)— E system of ordinates.
- (b) on a ν (f) — E system of ordinates.
- (c) on a λ (mμ)—% transmission system of ordinates. (See Table IX for the necessary conversion values of E .)

(d) Dot in on (a) and (c) the approximate curves for a solution of $\frac{1}{2}$ the concentration of the original sample.

2. (If Exercise 10 is omitted, the problem at the end of that exercise should be introduced here.)

Cellophane Samples. At the back of this book are inserted samples of several colored Cellophane films for which visual absorption spectra curves are given in Figs. 12.30 and 12.42. Although the extinction values may vary in these samples owing to slight changes in concentration of dye or thickness of the film, they may be useful as unknowns in the determination of absorption spectra in the visible or ultraviolet.

SUPPLEMENTARY EXPERIMENT

A number of spectrophotometers are so constructed as to permit the observation of reflection as well as absorption spectra (Fig. 12.31). The

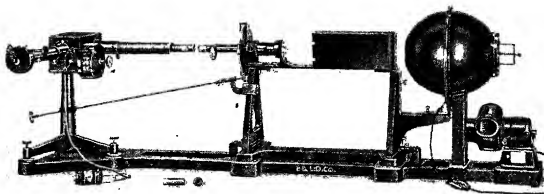


FIG. 12.31.—Reflection spectrophotometer (Bausch and Lomb).

reflection curves are usually broader than absorption curves, and hence one does not need to make observations closer than 10 $m\mu$. The procedure of observation is essentially the same as in the determination of visual absorption (i.e., setting the wavelength to definite values and adjustment of the extinction to a match of the two beams). The comparison sample in the case of reflection may be a piece of undyed or colorless material of the same sort as the sample under test, or the standard white produced by a magnesium carbonate block.

Since most reflection spectra are taken in connection with color analysis it is usual to record the data in percentage of light reflected (equivalent to percentage of light transmitted by transparent samples). It is suggested that the data obtained in this experiment be converted from extinction to percentage reflected. See Table IX for conversion values.

FIG. 12.32

SPECTROGRAPHIC LABORATORY

No.

VISUAL SPECTROPHOTOMETRIC ANALYSIS

Sample (1) *Orange 543-0*

Reflection Spectra

Observer

(2) *Blue Violet 248-BV*

Date

Comparison MgO

	(1)					(2)					(1)					(3)			
	Extinction			Av.		Extinction			Av.		Extinction			Av.		Extinction			Av.
440	0.50	0.55	0.54	0.53		0.21	0.18	0.27	0.22		590	0.00	0.00	0.01	0.00	0.68	0.71	0.70	0.70
(682)											(609)								
450	0.54	0.56	0.63	0.58		0.29	0.21	0.24	0.25		600					0.75	0.74	0.75	0.75
(667)											(500)								
460	0.64	0.61	0.69	0.65		0.32	0.28	0.26	0.29		610					0.71	0.73	0.75	0.73
(652)											(498)								
470	0.66	0.67	0.70	0.68		0.30	0.29	0.33	0.31		620	0.00		0.00		0.70	0.66	0.67	0.68
(638)											(484)								
480	0.69	0.65	0.72	0.69		0.34	0.42	0.37	0.38		630					0.59	0.65	0.63	0.62
(625)											(476)								
490	0.64	0.66	0.69	0.67		0.46	0.35	0.42	0.41		640					0.47	0.50	0.55	0.51
(618)											(469)								
500	0.68	0.62	0.65	0.65		0.52	0.45	0.43	0.47		650	0.00		0.00		0.36	0.40	0.44	0.40
(600)											(462)								
510	0.67	0.62	0.67	0.65		0.53	0.50	0.51	0.51		660					0.32	0.37	0.29	0.33
(588)											(455)								
520	0.64	0.63	0.63	0.63		0.57	0.59	0.56	0.57		670					0.32	0.26	0.22	0.27
(577)											(448)								
530	0.58	0.58	0.57	0.58		0.63	0.64	0.65	0.64		680					0.20	0.21	0.25	0.22
(566)											(441)								
540	0.47	0.50	0.48	0.48		0.67	0.67	0.68	0.67		690	0.00		0.00		0.13	0.20	0.16	0.16
(556)											(435)								
550	0.36	0.37	0.36	0.36		0.68	0.67	0.69	0.68		700					0.20	0.09	0.10	0.13
(546)											(429)								
560	0.24	0.26	0.23	0.24		0.65	0.66	0.66	0.66		710								
(536)											(423)								
570	0.08	0.12	0.10	0.10		0.66	0.68	0.65	0.66		720								
(526)											(417)								
580	0.02	0.00	0.04	0.02		0.67	0.69	0.67	0.68		730								
(517)											(411)								

EXERCISE 9

DETERMINATION OF ULTRAVIOLET ABSORPTION SPECTRA

Ultraviolet absorption spectra may be determined on a medium spectrograph (Bausch and Lomb, Hilger, etc.) to which has been attached a suitable photometer (Hilger sector photometer, Bausch and Lomb sector photometer, Hilger Spekker photometer, etc.) (Fig. 12.34).

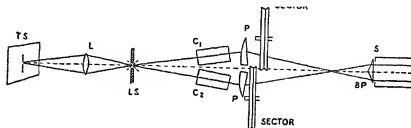


FIG. 12.34.—Sector photometer (Hilger).

Light Source. Although in many laboratories a simple steel arc is used as a light source, a continuous light source has been found to be more satisfactory. Two types of continuous light sources are available, the hydrogen discharge and the underwater spark (C79). As in the case of

FIG. 12.35

SPECTROGRAPHIC LABORATORY

PLATE RECORD

Serial Plate No. *.

Observer.....No.†.....

*Serial Plate-record book must be signed for each plate. *Observer number* must be indicated if *serial number* is not used on plate.

ANALYSIS FOR.

†Note: Use initial or other symbol to avoid confusion with serial number, i.e., W-10. *Observer number of serial number* must be written on plate.

Instrument.....

Date.....

	√	mm.	Sample	Time	Slit	Focus	E	E-0.3
1								
2								
3								
25								

the simple arc spectrum adjustment on the apparatus (Exercise 1), the optical line can be easily determined by placing an electric lamp at approximately the position of the red end of the plate holder, opening the slit to about 0.2 mm, and projecting a beam of light through to the focusing test screen.

Photometer. The specific directions given below are for a modified

Hilger sector photometer and medium Bausch and Lomb spectrograph. Other photometers work on the same principle with a few variations in construction. This photometer involves the separation of the light into two beams, one of which passes through the absorbing substance, while the other passes through the solvent and an adjustable rotating sector or other photometric device. By taking a series of photographs at different settings of this sector, it is possible to approximate the same effect as would be obtained on the visual machine by setting the extinction to a given value and moving across the spectrum by adjustment of the wavelength drum. At any point in the spectrum where the transmission of the absorbing material is the same as that of the rotating sector, the two beams will match. If one records these sector or photometer values, it will be possible to plot the absorption against the wavelength or frequency and thus to obtain the absorption spectrum of the absorbing substance.

Experimental Procedure. The observations are to be recorded on a plate record sheet (Fig. 12.35), and are to be made in the following manner: the first photograph taken at a setting of 0 is to be a scale; the second at 4 mm, a comparison photograph in which the cells are not placed in the apparatus and in which both sectors are open and stationary or diaphragms are set for complete transmission. This comparison photograph will indicate whether the two beams are in proper adjustment. The two cells are now placed in their proper positions, the bottom being inserted first. The cell in the beam from the fixed sector or diaphragm should be the solution of the absorbing compound, and the cell in the other beam should be the solvent. The sector or photometer diaphragm in front of the solution cell should be at 0 extinction (completely open) and the solvent sector or photometer at an extinction value of 0.1. The third photograph now should be taken at a millimeter setting of 8, and each succeeding photograph should be taken at successive settings of +4 mm each. The fourth photograph is taken as before with both sectors running, but with the extinction on the solvent sector set at 0.2. The fifth photograph would normally be taken in the same manner with the extinction set at 0.3 for the solvent (top) sector, and at 0 for the bottom sector with both sectors running.

Variation in Procedure with Sector Photometers. With certain types of two sector photometers (Hilger or Keuffel and Esser) a modification in the usual procedure is possible at this point. An examination of the percentage values equivalent to the extinction units will show that an extinction of 0.3 is equivalent to 50 per cent transmission. It is thus possible to remove the belt from the bottom sector, to leave it open and stationary, and to subtract 0.3 from the readings on the solvent (top) sector and

have the same relative transmission, so that, starting with photograph 5, the solution (bottom) is set at open and remains stationary, and the top sector is set at 0.3 less than the indicated extinction, or, in this case, 0. The sixth photograph is obtained by moving the plate holder down an additional 4 mm, setting the top sector at 0.1 ($E = 0.1 + 0.3 = 0.4$), and leaving the bottom one stationary.

Experimental Procedure (continued). Photographs are continued at every 4 mm with increase in extinction values of 0.1 at each exposure up to an extinction setting of 1.4 (equivalent to a sector setting of 1.1 in the modified procedure). The sector values by the modified method are recorded in the column $E - 0.3$ in the data sheet, the true extinction being this value plus 0.3. The two cells are now interchanged, the solvent being placed in the bottom beam and the solution in the top beam. The top sector is left open and stationary, and successive photographs are made at extinction values on the lower sector of 1.0, 0.5, and 0.0. Both cells are now removed, both sectors set at open, and a photograph taken for comparison of the two beams (this should be at a millimeter setting of 76). The last photograph (millimeter setting of 80) should be a scale photograph.

Exposure Time. The exposure time will vary, depending upon the curve and the extinction value. The exposure time is also a function of the intensity of the light source at the slit and the sensitivity of the photographic plate. For example, the comparison photographs may be made at exposures of 5 seconds, and the extinction photographs be started at 5 seconds for the lowest extinction value and increase in time as the extinction increases so that the highest value (for 1.4 extinction) should approximate 1 minute. The following table may serve as an example:

Extinction	Exposure Time (seconds)	Extinction	Exposure Time (seconds)
0.0	5	0.8	16
0.1	5	0.9	20
0.2	5	1.0	25
0.3	5	1.1	31
0.4	6	1.2	40
0.5	8	1.3	50
0.6	10	1.4	64
0.7	13		

If one knows that the compound does not have an absorption band in the extreme ultraviolet, or the extinction of the extreme ultraviolet band is low, it is quite permissible to reduce the exposure times at the higher extinction settings.

The above technique, indicated for a particular type of equipment, is

equally applicable to other ultraviolet spectrophotometers employing the photographic principle. In some of these, such as the Hilger Spekker photometer and the Bausch and Lomb sector photometer, there is no

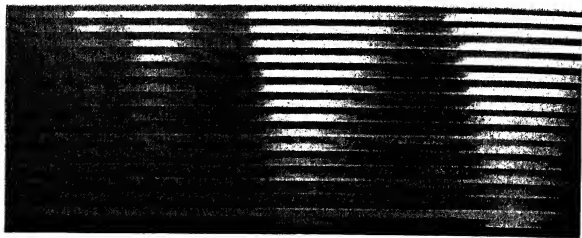


FIG. 12.36.—Partial spotting of negative.

provision for the increase of light and decrease of exposure time by the use of an open beam in the solution path, or for the interchange of solu-

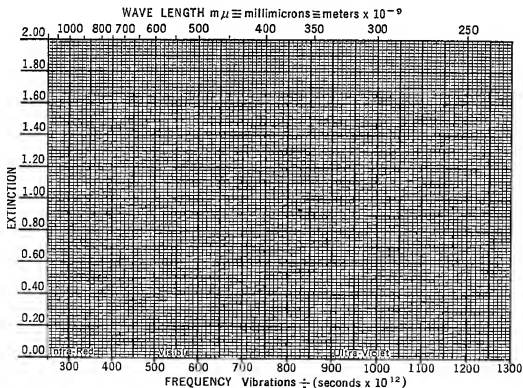


FIG. 12.37.—Form for graphical recording of ultraviolet spectrophotometric data.

tion and solvent so as to correct for any instrumental error in adjustment or light path. With these photometers one should make about the same number of exposures (the actual number is determined by the limits of

REPORT OF DATA

plate motion and size of the biprism or diaphragm at the slit), i.e., the extinction should be varied from 0.0 to 1.5 to 1.8.

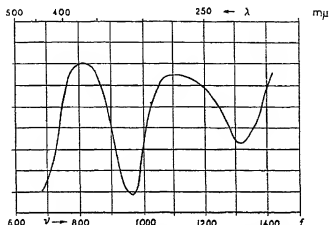


FIG. 12.38.—Potassium dichromate (frequency scale—see Fig. 8.52 for wavelength scale).

Spotting and Reading of Plate—Report. The plate is developed in the usual method, and when it is dry the match points are to be spotted.

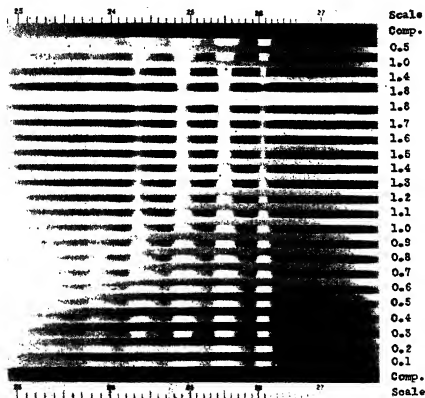


FIG. 12.39.—Absorption spectrum of benzene, $c = 2.64$ cg per liter, $d = 0.4$ cm. Extinction values as indicated.

This is done on the glass side so that the spots may be removed, and not on the film, a dot being placed on the dividing line between the two

beams whenever they have the same intensity (Fig. 12.36). If it is desirable to plot the curve in wavelength values, they may be read off directly by means of the printed scale; but, if frequency values are to be plotted, a special plate with a frequency scale (see Fig. 8.51) should be set on top of the plate, and the values read off directly in frequency units. These values are to be recorded on the data sheets and then plotted on the appropriate graph form (Fig. 12.37).

Standard Samples and Unknowns. It is suggested that a solution of

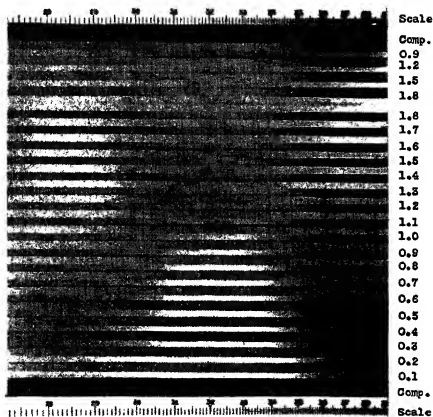


Fig. 12.40.—Absorption spectrum of cod-liver oil, $c = 0.0057$ gram per 100 ml, $d = 0.4$ cm. Extinction value as indicated.

$K_2Cr_2O_7$ (C101) (Fig. 12.38), azobenzene (C12) (Fig. 8.2), benzene (Fig. 12.39), or cod-liver oil (Fig. 12.40) be used for the analytical specimen. The concentration (c) of these solutions will depend upon the thicknesses (d) of the cells which are supplied with the photometer. The glass ring cells with quartz cover plates will be found to be very convenient for this work. The cover plates can be held on by spring clip, rubber tubing, or metal frame. (See Figs. 8.35, 8.36, and 8.37.)

Problems. 1. Using the film negative No. 2-G, in the pocket in the back of this book, spot the match points (*not* on the gelatin side), lay the negative on the reproduction of the reading plate (Plate XXXVII) (note that in actual practice a transparent reading plate is used), and record the frequency values of the match points.

For the plotting of these data the following information is essential: Sample of Hydron Orange (6,6-diethoxythioindigo) in CHCl_3 ; concentration = 1.25 cg per liter, cell thickness = 1.0 cm; photograph order bottom to top: (1) scale; (2) comparison; (3) $E = 0.0$; (4) $E = 0.1$. . . (19) $E = 1.6$; (20) $E = 1.8$; (reversed cells from this point on) (21) $E = 1.5$; (22) $E = 1.3$; (23) $E = 1.1$; (24) $E = 0.8$; (25) comparison; (26) scale.

2. The illustration (Fig. 12.40) is that of the absorption spectrum of a sample of vitamin A concentrate (cod-liver oil). Taking the extinction of the absorption band at 328 $\text{m}\mu$ as characteristic of vitamin A, and assuming that the photographs were made in the same order as the above sample, i.e., scale, comparison, 0.1, 0.2, 0.3, 0.4, 0.5 E , etc., up to the cell reversal point, determine the extinction of the maximum of the curve and from the factor

$$(\text{at } 328 \text{ m}\mu) E_{1 \text{ cm}}^{1\%} \times 2200 = \text{International Vitamin A Units}$$

calculate the vitamin A concentration of the oil from the above and the following data: concentration = 0.0057 gram per 100 ml; cell thickness = 0.4 cm.

3. The illustration in Fig. 12.39 is that of the absorption spectrum of benzene in alcohol, concentration = 2.64 cg per liter, cell thickness = 0.4 cm. Spot the match points in this figure, and, from the extinction values given at the side and the wavelength scale at the top and bottom, record and plot the absorption spectrum.

EXERCISE 10

PHOTRONIC COLORIMETERS

Electrical and Optical Principle. In recent years a number of photronic cell photometers and colorimeters have been developed for the measurement of the color intensity of colored liquids or glasses by transmission, or papers and solids by reflection. In all these instruments the optical system as shown in Fig. 11.8 is usually employed, with certain modifications for reflection measurements.

The current from the photronic cell is usually coupled to a microammeter with a shunting resistance which is variable in definite steps. By means of a suitable cell, ammeter, slide resistance, and step resistance, intensity variations from 1 to 10,000 can be easily measured with an accuracy of about 4 per cent.

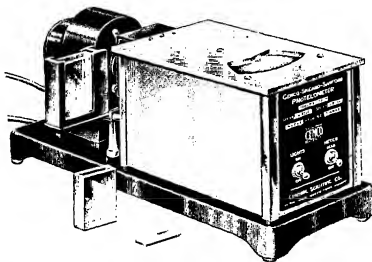


FIG. 12.41.—Photronic colorimeter (Central Scientific Company).
(See Fig. 11.8 for optical diagram.)

A slide resistance enables the operator to adjust the reading to a unit value such as 200, 500, etc., when it is desired to measure one substance against another to determine relative differences. A step resistance provides a means of measuring intensities quantitatively.

Some instruments have an exponential microammeter to provide a wide range with increasing accuracy at lower values so as to avoid the use of sliding or step resistances. The construction of a suitable colorimeter is not difficult since the essential parts, microammeter and photronic cells, are easily available. In the absence of a suitable manufactured instrument of this type or one built in the laboratory, satisfactory measurements can be made in this experiment, as well as laboratory determinations of color values of solutions, by means of the ordinary photronic photographic exposure meter such as produced by Weston, General Electric, or Zeiss. A suitable diaphragm such as is provided with the

General Electric meter to transmit $1/10$ of the light permits a wide range of accurately measured intensities. In the absence of a diaphragm one can employ the simple optical bench relations of variation of intensity with the square of the distance from the source as a means of variation of incident intensity, rather than keeping the source and cell at a constant distance and varying the intensity by a screen.

Experimental Procedure. The cell should be placed at a fixed distance from the light source so that with the $1/10$ filter in position the needle should indicate a nearly maximum value. This value should be recorded, and then colored cellulose films such as the duPont Cellophane filters which are supplied with this book should be interposed between the light and the photronic cell (in the General Electric exposure meter immediately in front of the $1/10$ filter). If the value on the meter drops down to less than $1/10$ of the original reading or the capacity of the meter, then the $1/10$ filter should be removed. (Be sure that the direct light does not strike the photronic cell so as to cause the needle to swing beyond the indicated capacity of the instrument.) Readings are to be made on all the colored samples which are supplied. It is suggested that small pieces slightly larger than the opening of the colorimeter be attached or mounted in cardboard squares with an aperture of the proper size or between lantern slide glasses so as to permit their repeated use as filters and to provide convenient mounting in front of the photronic cell.

Application of Data. The object of this experiment is to demonstrate how a simple photronic colorimeter can be used as a spectrophotometer in the measurement of color shades and intensities. The principles involved in this exercise require the subdivision of the visual spectrum into segments and the measurement of the color intensity in each of these segments. This is essentially what is done in ordinary spectrophotometry, Exercise 8, except that in that exercise the spectral segments were determined by the ocular and entrance spectrometer slits and were of the order of 1 or 2 $m\mu$. In this exercise we will divide the visual spectrum into five or six color sections (quite satisfactory results in the description of color have been obtained by the division of the spectrum into only three primary colors [Chapter XI]).

Standard colored glasses (Fig. 11.10), filters, or the colored Cellophane samples in this book may be used as the dividers of the visual spectrum (Fig. 12.30). The object of this experiment is to demonstrate certain spectrophotometric principles of color measurement, and workers are cautioned against the use of uncalibrated filters for very exact colorimetric analysis. Even though every effort has been made to obtain uniform filter samples it is, of course, difficult in the production of large quantities of relatively inexpensive colored films to maintain an accurate

control on the dye strength or thickness, and sometimes the dyes themselves may fade on continued exposure to light. In the application of these filters it will be necessary to know the spectral transmission curves which are given in Fig. 12.42 together with the relative visibility curve of the eye.

An examination of the extinction curves of these Cellophane filters will indicate that double-thickness pieces of the yellow, orange, and red and

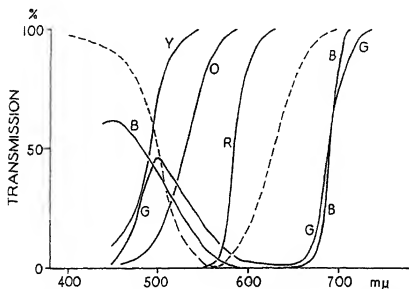


FIG. 12.42.—Transmission curves of colored Cellophane samples. (See Fig. 12.30 for extinction curves.) (Dotted curve indicates relative visibility.)

single-thickness pieces of the green and blue will provide a better subdivision of the spectrum than that obtained by the use of single-thickness filters for all colors. In addition it will be noted that both the blue and green filters have a transmission region in the far red portion of the spectrum. The use of a combination blue and red filter or a green and red filter will provide an additional spectral segment which should be included in the series of observations made with these Cellophane filters, and values obtained with both the green and the blue filters should be corrected by the subtraction of the extreme red transmission value obtained by this combination blue (or green) and red filter. The following dominant wavelength values are suggested for the Cellophane filters:

Blue (1×).....	470 mμ
Green (1×).....	510
Yellow (2×).....	560
Orange (2×).....	600
Red (2×).....	660
Red (2×) + Blue (1×).....	690

In the use of these values it should be remembered that the corrected orange value of $600\text{ m}\mu$ represents the difference in transmission between the orange and the red filters, or the spectral segment which is transmitted by the orange but not by the red filter. A similar correction has been applied in the assignment of the corrected yellow value, in that this represents the spectral segment which is transmitted by the yellow but not by the orange filter.

The indicated dominant wavelength values for the green and blue filters require a similar correction in the form of subtraction of the red + green (or blue) transmission from the green (or blue) transmission. The spectral segment obtained by the use of the red + blue filter ($690\text{ m}\mu$) is so near the limit of visual perception that it may be neglected in the subdivision of the spectrum for visual color analysis. The values obtained for this far red segment should, however, be applied as correction values to the blue and green filter observations.

The data obtained by the direct measurement of the transmission intensity of the set of five filters (red, orange, yellow, green, and blue, but not purple) should be compared with the transmission curves given in Fig. 12.42. It may be assumed that these filters divide the visual spectrum into five sections of approximately equal range with dominant wavelengths characteristic of each color. If the total intensity of the white light is observed as 500 foot-candles, and it is assumed that the energy distribution of the white light is about equal over the visible wavelength range, then one may assign to each of the component colors $1/5$ of this value, or 100 foot-candles, to each region. From an examination of the transmission curves of the red, orange, and yellow filters (Fig. 12.42) it can be seen that the yellow filter transmits all the red and orange light as well as the yellow, and the orange filter transmits the red as well as the orange, hence the spectral yellow value (Y_0) will be equivalent to the observed filter yellow value (Y_1) less the observed filter orange value (O_1); i.e., $Y_0 = Y_1 - O_1$, and in like manner $O_0 = O_1 - R_1$. If the observed yellow, orange, and red values for the filters measured against a white light are $Y_1 = 310$, $O_1 = 215$, and $R_1 = 105$, then the spectral values for these three colors will be $Y_0 = 310 - 215 = 95$; $O_0 = 215 - 105 = 110$; and $R_0 = 105$.

The intensity factor and dominant wavelength may be determined for each color by the area and the center of the surface bounded by the absorption curve of the filter and the relative sensitivity of the eye curve (Fig. 12.42). In the case of compound colors such as yellow, which in the filter includes both orange and red, the dominant wavelength of the spectral yellow is determined by the area bounded by the absorption curve of the yellow filter, the absorption curve of the orange filter (whose

energy is to be subtracted from the yellow value), and the visibility curve (Fig. 11.1).

For the filters shown in Fig. 11.10 the following assignments of dominant wavelength may be used: red = 660 m μ , orange = 610 m μ , yellow = 575 m μ , green = 530 m μ , blue = 470 m μ . The student should compare the transmission curves of his filters (Fig. 12.30) with the above assignments and filter curves and make his own division of the visible spectrum. The original assumption that each filter could be considered as transmitting the same amount of spectral energy was based on an assumed division of the spectrum into five equal energy regions and an assumed 100 per cent transmission of the energy in this region by the filter. Certain filters, especially the green, have an appreciable absorption in the region of maximum transmission or dominant wavelength. It will therefore be necessary to multiply all values observed with this filter by a constant so as to bring readings taken with this type of filter to the same basis as the other filters.

It may also happen that the area of transmission of (or energy transmitted by) one of the filters may be greater than the assigned 1/5 of the spectral region, and hence it will be necessary to correct this filter value by multiplying by a factor of less than 1 to bring its readings to the same basis as the other filters. For example, if the green filter gives an energy transmission of 45 and the blue filter a value of 135 foot-candles, where the original white light reading is 500 and the division into equal energy would give 100 foot-candles to each spectral region, the correction factor for the green will be 100/45 or 2.22, and the correction factor for the blue will be 100/135 or 0.74. It is thus possible to measure a white-light source with photometer and determine the total energy and, by repeating the measurements with the set of filters, to assign relative intensities to each of these filter spectral regions. These values should all be equal and represent 100 per cent transmission for each of these regions.

Measurement of Unknowns. If a colored glass, solution, or one of these filters (it is suggested that the green or purple filter be used) is to be measured, it should be placed in front of the photronic cell and its total transmission measured. It should then be placed with each of the five filters in turn in front of the cell and the spectral transmission with the filter determined. The corrected values for the spectral regions, when added together, should be approximately the same as the original total transmission of the filter (based on the assumption that the five-way division by the filters is in approximately equal energy distribution).

Dividing the corrected values for the white light for each filter into the corrected values for the interposed sample for the corresponding filter one can obtain the percentage of light transmitted in each spectral re-

gion. These values should be plotted and the transmission curve indicated from the five points. The observations on the above two samples (purple and green filters) should be repeated for a three-thickness piece of the sample.

Report. The final report should include a data sheet indicating:

(a) Total energy or light intensity of source (this may be an extrapolated value by use of a 1/10 or other reducing filter if the original source is too bright for direct measurement).

(b) A tabular indication of the values for each filter, dominant wavelength, correction factor, corrected values, and total energy by summation of filter segments.

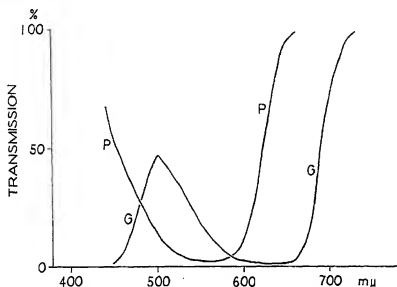


FIG. 12.43.—Transmission curves of colored Cellophane samples. (See Fig. 12.30 for extinction curves.)

(c) A tabular indication of the values for each unknown or test sample for each filter, the corrected values, percentage transmission, total energy by summation, and direct total energy (test sample without filters).

(d) Graphical representation of the transmission spectra of the test samples.

Although the experiment which has been described deals with the transmission spectra of samples, it should be kept in mind that similar instruments are available for the determination of reflection spectra. If the photonic cell instrument, such as a photonic exposure meter, is not graduated in foot-candles or other direct measure of luminosity energy, it may be necessary to calibrate the scale by setting the instrument at definite distances from a test lamp and applying the principle of variation of energy with the square of the distance in the calibration of the scale. The calibration need not be in foot-candles, since the final

values recorded and plotted are percentage values based on the ratio of two readings of the instrument.

Problem. From the data given in Figs. 12.30 and 12.42 or observed data in this experiment prepare curves (extinction and percentage transmission) showing the effect of combining the following filters: (a) purple and red; (b) green and yellow; (c) yellow and red; (d) blue and green; (e) blue, green, and yellow; (f) double thickness of orange.

From an examination of these curves and the observed data, suggest combinations to provide additional or better segmentation of the visible spectrum by these filters.

Note: It should be remembered, in the addition of absorption effects, that extinction curves can be directly added together but that percentage transmission curves cannot be directly added to obtain the compound curve (see Table IX for the relation between extinction and percentage transmission).

EXERCISE 11

SPECTRAL TRANSMISSION OF GLASS AND PLASTIC SAMPLES

In its original form this experiment was intended to be performed with an ultraviolet hand spectroscope (Beck) (Figs. 12.44*a* and 12.44*b*) having an iron arc as the ultraviolet source. The spectra as observed through the eyepiece appears as one of the strips in the following photographs (Fig. 12.45). The illuminated scale is a part of the optical system of the spectroscope. The ultraviolet hand spectroscope has a fluorescent screen

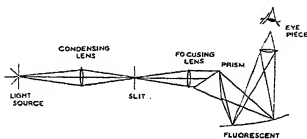


FIG. 12.44*a*.—Hand spectroscope for ultraviolet (diagram).

upon which the spectra and the scale are projected and upon which the eyepiece is focused. It operates, in principle, much the same as a visual hand spectroscope, and, in laboratories in which an ultraviolet hand spectroscope is not available, the experiment will have to be confined to visually colored plastics, glasses, and solutions.

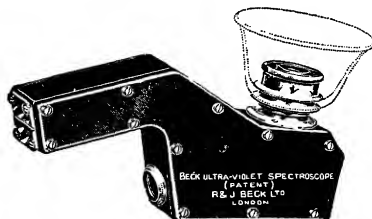


FIG. 12.44*b*.—Hand spectroscope for ultraviolet (Beck).

In order to illustrate the ultraviolet absorption of some common materials the photographs in Fig. 12.45 are given. It is suggested that an estimate be made of the ultraviolet transmission of these samples as well as the samples which are provided for test. For ultraviolet measurement the following samples are suggested: various grades of plate and window glass, Vita glass, Corex, Uviol, Pyrex, microscope slides, Cello-

phane, Pliofilm, cellulose acetate, Celluloid, Vinylite, Bakelite, etc. (for thin films it may be necessary to use several thicknesses).

Caution: Avoid looking directly at any ultraviolet light source.

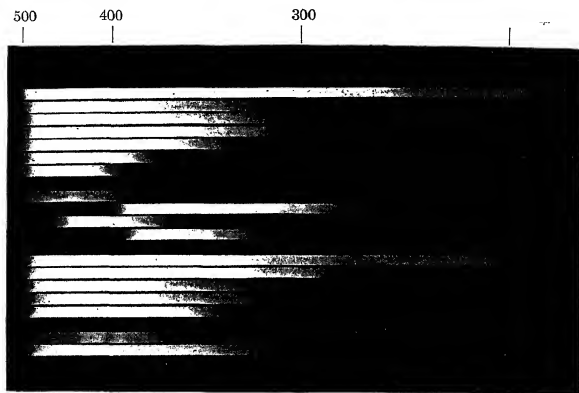


FIG. 12.45.—Spectrograms of transmission samples (continuous source from under-water spark). (See Table 12.7 for identification code.)

The data should be reported as follows (this partially completed data sheet provides the necessary information for the analysis of the observations in Fig. 12.45):

TABLE 12.7

ULTRAVIOLET TRANSMISSION OF MISCELLANEOUS SAMPLES

Plate No.	(See Fig. 12.45)		Observer.....	
No.	Check	Sample	Thickness	Range of Transmission
1	✓	Scale		
2	✓	Blank (quartz)		Visual to 2950†
3	✓	Luster glass	2.3 mm
4	✓	Microscope slide	1.3 mm
5	✓	Pyrex	2.6 mm
6	✓	Plate glass	6.0 mm
7	✓	Greenish nultra	2.5 mm
8	✓	Noviol	3.6 mm
9	✓	Sextant green	3.5 mm
10	✓	Dark shade Alko	2.6 mm
11	✓	Red purple Corez A	5.5 mm

TABLE 12.7 (Cont.)

12	✓	<i>Blue (No. 14)</i>	<i>2.2 mm</i>
13	✓	<i>Blue (312-UC2)</i>	<i>1.9 mm</i>
14	✓	<i>Blue (493-BG6)</i>	<i>2.5 mm</i>
15	✓	<i>Cellophane (1×)*</i>	<i>0.02 mm</i>
16	✓	<i>Cellulose acetate (1×)</i>	<i>0.02 mm</i>
17	✓	<i>Pliofilm (1×)</i>	<i>0.02 mm</i>
18	✓	<i>Celluloid</i>	<i>0.2 mm</i>
19	✓	<i>Methylmethacrylate</i>	<i>72.3 mm</i>
20	✓	<i>Red Cellophane (1×)</i>	<i>0.02 mm</i>
21	✓	<i>Neodymium glass</i>	<i>10.1 mm</i>
22	✓	<i>Zeiss GO filter</i>	<i>1.5 mm</i>
23	✓	<i>Scale</i>	

* Single thickness = 1×.

† Method of reporting observations.

EXERCISE 12

QUALITATIVE AND SEMIQUANTITATIVE SPECTROPHOTOMETRY
PHOTOGRAPHIC PLATE SPECTRAL CALIBRATION

Apparatus. The apparatus for use in this experiment can be constructed from easily available parts (Fig. 12.46).

The light source ($L.S$) may be a T-20 type prefocus-base projection bulb (110-volt, 200-watt) or a single-filament lamp of the street-lighting series type (10 volts, 6 amperes) (which can be run from a Jefferson toy or miniature electric train transformer). A more suitable though more expensive source is the single-wire galvanometer lamp. The filament is focused (L_1) as a line source on the density wedge (W) or step slit (S),

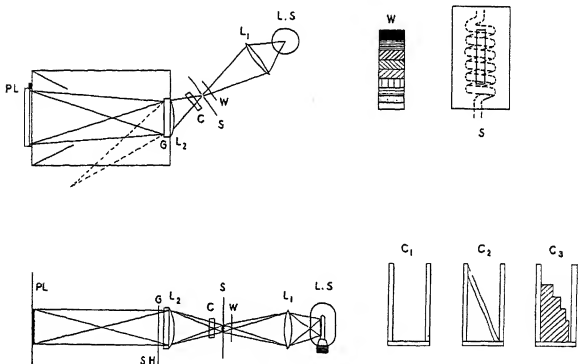


FIG. 12.46.—Wedge grating spectrograph.

adjacent to which is the cell (C) which can be used for spectral measurement of solutions; the cell can be replaced by filters or glasses if one wishes to measure the transmission of solid samples.

The grating and second lens are indicated by G and L_2 in the above diagram. The grating is a transparent replica grating such as is produced by casting a collodion image of a ruled grating and mounting it on glass. The second lens is placed so as to bring line spectra, produced by the substitution of a neon tube for the light source, into focus at the plate holder (PL). The plate holder has a permanently mounted glass plate immediately in front of it which is transparent except for a photograph of coordinate rulings and a scale which is printed on the bottom and projects onto the photographed spectrogram as a calibration background

(Fig. 12.47). It may be necessary to dye a portion of this screen plate a light yellow to absorb second order images from the grating in the red end of the spectrum.

Experimental Procedure and Reports. The following experiments are suggested:

(a) Determine the spectral sensitivity of a film or plate by exposure with the density wedge. The print of the wedge spectrogram should be mounted and properly labeled to indicate the type of plate and character of spectral sensitivity. If available, additional films might be tried, keeping the exposure time uniform. The plate holder can be constructed so as to permit the use of motion-picture (35-mm) film, which is easily available in a wide variety of types, including infrared-sensitive.

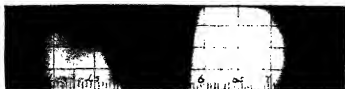


FIG. 12.47.—Wedge spectrogram of Rose Bengal 5B 1/400 (Mees [B 39]).

(b) Determine the spectral transmission of the colored films supplied in this book, using a panchromatic film for photographic observation. The report should include prints of the spectrograms mounted above approximate extinction curve diagrams reduced to the same dispersion. (These curves can be obtained from the extinction data given on these films in Fig. 12.42.)

(c) Determine the spectral transmission of a solution of potassium permanganate or crystal violet, reporting as above and comparing the spectrogram with the data on the same solution obtained in Exercise 8.

LECTURE DEMONSTRATION

DEMONSTRATION OF ABSORPTION SPECTRA AND COLOR FORMATION

The method described below has been used with considerable success in the lecture demonstration of absorption spectra and color formation. It also forms the basis for a colorimeter by means of which one can produce a color match or color analysis of the most complicated type. In its simpler form this colorimeter can be used with three fixed absorbing bands as a trichromatic colorimeter, or with one or two movable bands it can simulate with accuracy practically all the simple absorbing effects which produce visible color.

The light source (*LS*) recommended for this experiment is a T-20, 500-watt projection bulb. A straight single-filament bulb taking 6 volts,

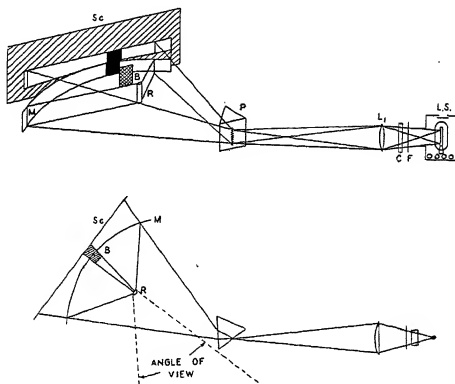


FIG. 12.48.—Demonstration of absorption spectra.

10 amperes, might be better, but such a current supply is usually not so conveniently obtained as the 110-volt current. The bulb should be placed in a protected ventilated housing so that the filament is viewed from the side as a single line. This is focused by a lens (L_1) so that the point of focus of the image will be at the prism (P). This prism can be a solid glass 60° type, or a hollow glass prism made by cementing glass plates together on a flat plate, the edges of the plates being beveled so as to form a smooth cemented joint with the water-glass cement. A hollow glass prism of this type with a ground-glass stopper can be obtained from the usual laboratory supply houses. The prism should be filled

DEMONSTRATION OF ABSORPTION SPECTRA

with carbon disulfide, which has a high refractive index and will produce a spectrum with a reasonably high dispersion.

The spectrum, since it is produced from a nearly parallel beam of light owing to a short-focus lens placed close to the light source, may be considered as originating as approximately a line source at the prism and will be essentially in focus at any point at which one might desire to put the viewing screen (*Sc*). With the light source placed about 10 feet from

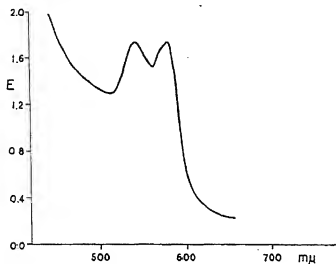


FIG. 12.49a.—Absorption spectrum of hemoglobin.

the prism and the card at about an equal distance on the other side of the prism, a spectrum about 4 feet in length and about 8 inches high is produced in sufficient brilliance to be easily viewed in a large lecture room. Immediately in front of the viewing card is placed a cylindrical mirror (*M*). For modern plate-glass windows a technique of manufacture has been developed for producing curved plate glass with a radius of curvature of 10 to 15 feet, and in the installation of such pieces it is usually



FIG. 12.49b.—Filter strip to produce a blood-red color.

necessary to cut off narrow strips. A strip of such a plate-glass piece, about 3 or 4 feet long and 4 inches wide, can be silvered by rocking in a silvering tray, much as one would develop a photographic film; it then forms an excellent cylindrical mirror for this demonstration. This cylindrical mirror should be mounted in such a manner that it collects about half the height of the spectrum on the viewing screen and allows the remainder to pass over the top of it and be visible to the audience. The collected image from the cylindrical mirror will be focused at the point

(*I*) in the form of a line of light which represents a recombination of the spectrum into a single color. If a focusing screen (*R*) is placed at this point it will be possible to see this effect, provided that the focusing screen does not obstruct the spectrum on the mirror and card. Such a screen can be produced by grinding a 1/8-inch-diameter, 5-inch-length piece of solid glass rod to a half-round cross section and focusing the light on the back or ground-glass flat face. The placing of this rod at the focal point involves a rather critical adjustment but is not difficult. The cylindrical smooth side of the rod will give a brilliant image of the ground-glass back face over a considerable angle of view.

The placing of glass filters (*P*) or colored solutions in cells at the point *C* will cause the absorption spectrum to appear on the test card with a dark band where the light is absorbed, and the color of the light transmitted by the glass or solution will appear on the focus rod (*R*). That the color at *R* is the same as the transmitted color of the glass can be easily demonstrated by placing a card at *P* so as to show this color. A number of black cards (*B*) about 10 inches in height and of varying width should be available and mounted on slotted wooden blocks so as to stand on the table. These strips, placed immediately in front of the cylindrical mirror, are equivalent in effect to an absorption band. The portion of the spectrum which is cut out by the card can be seen in the test screen, while the color produced by the elimination of that part of the spectrum by absorption is seen on the focus rod (*R*). The use of several cards or a glass plate with a shaded blackening with a dark streak in the center and gradual reduction in intensity towards the edge will produce a wide variety of effects. It is possible to prepare Celluloid strips the length of the spectrum and blackened in certain parts to produce gradual or total absorption and simulate such colors as blood red (Fig. 12.49) with considerable success.

CHAPTER XIII

THEORY AND PRACTICE OF PHOTOGRAPHY (*B43, A15*)

IMAGE FORMATION—EMULSIONS

The production of a photographic image on a negative or paper is dependent on the formation of a latent silver halide image by a photochemical action; the reduction of the latent silver halide image by a suitable developer to the metallic silver image; and the removal, by a suitable solvent or fixing agent, of the unaffected silver halide. The silver halide particles which are suspended in a gelatin emulsion are photosensitive, in that the particles which have been affected by light form a latent image and are sensitive to the action of the developer whereas those particles which have not been activated by light are insensitive to the developing agent.

The size of the silver halide particles, and the nature of additional components in the emulsion, such as photosensitizing dyes or thiourea, determine the density of the image which will be produced by a given light intensity under standard conditions of development. In Fig. 13.1 are given the density against logarithm of intensity ($d/\log I$) curves for two emulsion types. These curves will, of course, vary with different colors of light and developing conditions.

Fig. 13.2 shows the effect of increased time of development on the density of the image. A similar effect is shown in the change of temperature on the density of the image. As can be seen in these curves and in Fig. 13.3 there is a certain intensity or time period over which there is an increasing rise of d with $\log I$ or $\log T$. This is followed by a region in which there is a constant rise of density, and then this is followed by a region of decreasing rate of density increase. Eventually the rate of decrease results in a maximum density which is followed by lower densities with a complete destruction of the latent image or reversal of the image.

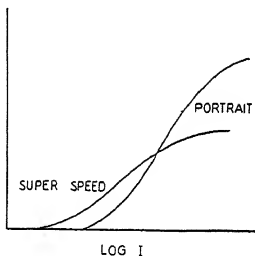


Fig. 13.1.— $d/\log I$ curves for different emulsion types.

The most satisfactory portion of the density curve, and the one within which the exposure should be made, is the straight-line portion of the $d/\log I$ curve. If one extends this straight-line portion of the $d/\log I$ (or $\log E$) so that it meets the ordinate axis of zero density, the intensity for constant time (or exposure time for constant intensity), which is indi-

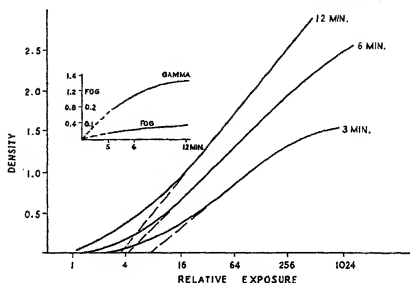


FIG. 13.2.—Increase in gamma (slope of straight portion of $d/\log I$ curve) with increased development time (Agfa Super Pan Press Film).

cated, is known as the inertia of the emulsion. In order to express conveniently the rate of increase of density with the logarithm of the exposure, the term gamma (γ) is employed. By definition, gamma is the tangent of the angle produced by extension of the straight-line portion of the sensitivity curve when it meets the axis of zero density. From Fig.

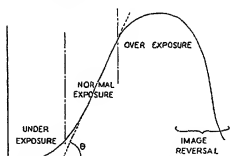


FIG. 13.3.—Extended $d/\log I$ curve indicating normal exposure range, inertia (i), gamma (γ) ($\tan \theta$ or slope of normal exposure), and image reversal caused by over exposure with a destruction of the latent image.

13.2 and other data it can be seen that the time of development, or temperature, directly influences the size of the gamma value for a given emulsion. Short exposure and long development will result in a high gamma value; low gamma, or low contrast, values are produced by long exposure and short development.

In order to repress "fog" in the developing process, it is customary to

add a small amount of potassium bromide. In the absence of bromide in the developer, the inertia of the negative or emulsion is constant for various times, but with the addition of bromides there is a depression of the inertia point to negative density values, which results, as indicated in Fig. 13.4, in an apparent increase in the inertia value, without a corresponding decrease in the gamma or contrast value. This means that weak exposures will produce little or no effect but exposures of normal intensity will produce nearly normal images.

Emulsions designed to give the greatest possible contrast, such as the process plate, have a very limited range (about 1 to 4), whereas soft negatives such as a portrait panchromatic may have a range of 1 to 250. The greater range indicates a greater possible variation in exposure time

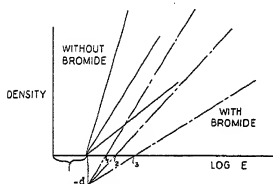


FIG. 13.4.—Effect of added bromide on chloride emulsions. Note increase of inertia without loss of gamma.

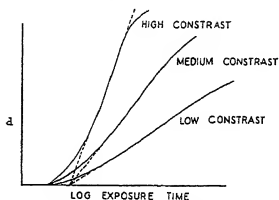


FIG. 13.5.— $d/\log I$ curves for low, medium, and high contrast paper emulsions.

or light intensity which can be observed in different densities on the photographic plate. This latitude is generally much greater in negative emulsions than in paper emulsions (Fig. 13.5).

DEVELOPING PROCESS

The developing process involves the use of a suitable reducing agent which will convert the latent silver halide to metallic silver, and the removal of the unaffected silver halide by a suitable solvent or fixing agent. As in the exposure of the silver halide, the development is preceded by an induction period. This induction period has been taken as a means of calculating the proper developing time in accordance with a formula by Watkins:

$$T = W \times T_a$$

where T is time for the production of proper density, T_a the time for first appearance of the image, and W a constant for the developer (including developing temperature). This method of factorial development may be

roughly applied to the common metol-hydroquinone developer by the use of a factor 10 to 12 times the time of first appearance of the image.

Nearly all the common developers contain, in addition to the organic developing agents, sodium sulfite or bisulfite, and sodium carbonate or hydroxide. The sodium carbonate or hydroxide acts as a solvent for the phenolic types of organic developers. With the introduction of basic developers, such as *paraphenylenediamine*, it is possible to change the *pH* to a more nearly acid condition. The true action of the sulfite is somewhat uncertain, although there is some evidence of its acting in part as a regenerator of the organic developer after oxidation and as a stabilizer of the reducing developer to prevent oxidation by the oxygen in the air.

For general spectrographic analysis it is suggested that the *Eastman 33* plates be used, and that development be made with an accepted metol-hydroquinone formula such as:

METOL-HYDROQUINONE DEVELOPER (Agfa 20)

Hot water (52° C).....	750 ml
Metol (elon).....	2 grams
Sodium sulfite, anhydrous.....	25 grams
Hydroquinone.....	4 grams
Sodium carbonate, monohydrated.....	18 grams
Potassium bromide.....	2 grams
Water to make.....	1 liter

Do not dilute for use.

TECHNIQUE OF DEVELOPMENT

In the development of the 33 plate in qualitative experiments and in many of the quantitative measurements, it has been found that the M-Q tube developer is satisfactory (see page 237). Developing time at 70°F will be about 2 minutes. In all developing processes, including both plates and paper, care should be taken that the negative or paper is completely and uniformly covered with the developing solution and that no air bubbles remain attached to the surface of the emulsion. If the tray of developer is lifted slightly on one edge so as to flow the developer to the other side of the tray and the negative inserted into the developer and the tray edge lowered, the developer will flow back over the negative to the other side. If the adjacent edge is now raised and lowered, the developer will flow at right angles to the first direction of flow and should completely and evenly cover the negative. Care should be taken not to touch or scratch the emulsion side and to hold the negative by the edges when it is necessary to handle it.

After complete development the negative or paper is transferred to a short-stop tray which contains about the same amount of liquid as the

developer tray, 250 ml for an 8 by 10 inch tray. This short-stop for negatives and paper prints should contain about 2 ml of glacial acetic acid. More of the short-stop acid will be necessary for paper prints since it is designed to neutralize the carbonate or alkali from the developer before the print is introduced into the acid hypo or fixer bath. In the development of fine-grain negatives one may find the use of chrome alum short-stop of advantage (3 grams potassium chrome alum, 3 grams sodium bisulfite, 250 ml water). The negative should remain in the short-stop for about 30 seconds (paper prints about 1 minute) before being placed in the fixing solution.

The fixing bath should be prepared according to the following directions, dissolving the chemicals in the order given:

SOLUTION 1

Water.....	2 liters
Hypo ($\text{Na}_2\text{S}_2\text{O}_3$).....	960 grams

SOLUTION 2

Water (52° C).....	600 ml
NaHSO_3 (anhydrous).....	60 grams
Acetic acid (28%)*.....	180 ml
Potassium alum.....	60 grams

Add solution 2 to solution 1, stirring rapidly.

* 28% acetic acid can be prepared from glacial acetic acid by adding 3 parts of acid to 8 parts of water.

Negatives should remain in the fixer for at least 10 minutes after the last visual trace of silver halide has disappeared. Prints should fix completely in 10 to 15 minutes. Agitation of developer and fixer is essential for even developing and fixing and is best accomplished by gentle rocking of the tray during the process. Agitation is more essential to development than to the fixing process. In the fixing of a number of prints one should move them about from time to time so as to avoid the stoppage of the fixing action which may be caused by two paper surfaces in contact.

The completely fixed negative or print should be transferred to a washing tray and washed in a slow stream of water at 18 to 21° C (65 to 70° F) for 15 to 20 minutes. The use of water which is warmer than this temperature range may cause the emulsion to soften unless it has been previously hardened. Colder water than this range will harden the gelatin and slow down the water penetration and thus necessitate a much longer washing period to remove all the hypo. After washing, the negative should be wiped with a soft, wet viscose sponge or cotton pad so as to remove surface dirt; this is especially true if hard water is used and a scum of calcium salts forms on the film surface. For rapid drying, the plate may be wiped with a moist viscose sponge, from which nearly all

the water has been pressed out, before it is placed in the drying rack. Prints should be dried between blotters or on ferrotype tins. The process in both methods of drying can be accelerated by an electrical drying unit.



FIG. 13.6.—Wedge spectrogram indicating emulsion sensitivity (Agfa Ultra Pan).

SAFELIGHTS

The choice of the negative emulsion (Eastman 33) in the experimental section was based in part on its ability to be used with a No. 1 Wratten safelight and thus permit its development to be more easily observed in class or student demonstrations. One should be certain that the proper safelight filter for the negative or emulsion has been inserted in the safe lamp, and, in case of doubt, especially with the panchromatic type of emulsion, it is advisable to use no safe lamp but develop in total darkness on a time basis. In the preparation of a safelight filter one should remember that many red dyes or filters transmit a considerable amount of blue or near ultraviolet and the apparent dark red color of a filter is not a guarantee that the filter will be suitable as a photographic safelight.

The amount of light that can be safely permitted in the development of bromide enlarging paper is considerably greater than most workers are accustomed to use. As with photographic emulsions on film or negative base, one must be certain that the safelight filter has a sufficiently sharp absorption band in the yellow and continues to absorb in the near ultraviolet. When there is doubt about the suitability of the safelight, the following test may be performed: cover half of a small piece of film or paper and expose the uncovered half to the safelight for a period of 2 minutes (the usual developing time in front of the safelight). Then develop for $1\frac{1}{2}$ to 2 minutes in darkness or with the emulsion side down in the tray. (N.B.: in normal development of films, plates, and paper always develop with the emulsion side up in the tray.) If the exposed half turns gray the safelight should not be used with that emulsion. It may be that a lamp of lower wattage in the safelight will reduce the fog sufficiently to permit the use of a given safelight filter.

ENLARGEMENTS

Enlarged prints for study or for reproduction purposes are best produced by means of a contrast glossy bromide paper such as *Eastman*

News Bromide (Contrast) or *Agfa Brovira* (Single-Weight Contrast). The exposure for an enlargement should be controlled by the lens diaphragm or by the time so that the developing time will be approximately $1\frac{1}{2}$ to 2 minutes for the production of full-scale tones. For greater contrast the exposure should be shorter and development time longer, or an extra amount of potassium bromide may be added and a longer exposure and development given to the print.

An objection to the use of paper enlargement for the measurement of line positions arises out of the uneven shrinkage of a paper print after exposure and before measurement. A special type of photographic paper has been developed for the reproduction of maps by the enlarging process (*Agfa Mapping Special*) in which nearly all shrinkage has been eliminated by special treatment of the paper stock. This paper with a high-speed bromide emulsion is well suited for the production of spectrogram enlargements for line identification by direct measurement.

For development of photographic enlargements the M-Q tube developer may be used, or the following formula is recommended (*Agfa 125*):

STANDARD BROMIDE PAPER DEVELOPER

Stock Solution

Metol (Elon)	6 grams
Sodium sulfite (anhydrous)	88 grams
Hydroquinone	24 grams
Sodium carbonate (monohydrated)	130 grams
Potassium bromide	4 grams
Water	2 liters

For use dilute 1 part of stock solution with 4 parts of water.
Normal developing time, $1\frac{1}{2}$ to 2 minutes at 21°C (70°F).

In the preparation of photographic prints it is recommended that the paper be handled with nickel, hard rubber, or wood tongs, care being taken that the developer tongs do not touch the hypo or short-stop solutions. The fingers are thus kept dry in the handling of the unexposed and exposed paper.

PHOTOGRAPHIC DARK ROOM

Fig. 13.7 is a dark-room plan which has been found to be satisfactory for routine analysis and group instruction (Fig. 13.8). Two safelights are provided, *SL-1* and *SL-2*, so that bromide prints and negatives can be worked without the necessity of changing safelight filters. The safelight switches should be placed on the wall immediately above each light so that they can be easily reached and turned in the dark. The developer (*D*), short-stop (*S*), and fixer (*F*) trays are indicated in their proper order, with the final wash tray (*W*) in the right-hand sink (*SK*). Immediately above the right side of the sink should be placed a paper-towel holder (*T*). It is desirable to keep a continuous flow of water in the sink

so that one can easily wash his hands and obtain a towel without touching a faucet. It is particularly essential that hypo should not be spilled or dropped on the table or floor, and hence the hypo tray should be placed adjacent to the sink; the hand should be washed immediately whenever it has been in the hypo. Although it is possible to turn on the room lights about 1 minute after putting a print or negative into the hypo tray, one should avoid picking the negative or print out of the tray to examine it on account of the danger of dropping hypo. The best practice is to let the negative or print fix in its normal reaction time and wash

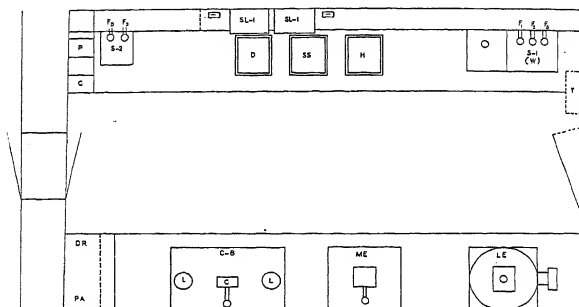


FIG. 13.7.—Photographic dark room showing (upper side) developer tray (*D*); short-stop tray (*SS*); hypo tray (*H*); wash tray (*W*) (in sink); safelights (*SL-1* and *SL-2*) with switches at side of each; sinks (*S-1* and *S-2*), (note cold [*F*₁], hot [*F*₂], and ice [*F*₃] water at *S-1* with mixing faucet to maintain uniform temperature of water at 65°–70°F); paper towel rack (*T*) next to sink. Above *S-1* are shelves for trays and developers; above *S-2* are shelves for plates and absorption cells: (lower side) enlarging machine for 10 inch negatives (*LE*), miniature (35 mm) film enlarger (*ME*), copy stand (*C-B*), plate drying rack (*DR*) and shelves for enlarging paper (*PA*). Below table tops on each side are shelves for developers and special materials.

it thoroughly before holding it up for close examination. The principal reason for this care with hypo is not on account of any corrosive action that hypo might have, but rather that hypo when it dries forms an efflorescent powder which will get into the air and will settle on negatives, plate holders, paper, and other apparatus that may come in contact with the sensitive emulsion, with resulting white dots or hypo marks in the final print or negative.

Additional equipment in a dark room should include two enlarging machines; one for the reproduction of large portions of a negative and capable of taking a regular 4 by 10 inch negative; the other should be of the miniature (35-mm) type and capable of enlarging a small portion of

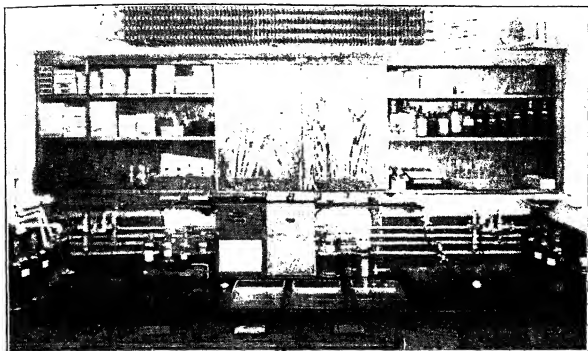


FIG. 13.8.—Developing side of dark room indicated in Fig. 13.7.



Ordinary



Orthochromatic



Panchromatic

FIG. 13.9.—Wedge spectra of photographic emulsions (Eastman Kodak [C 80]).

a negative to 10 or more times. It has been found very convenient, and in hot weather almost a necessity, to have running ice water (supplied from a drinking-fountain cooling system) and an air-conditioning unit in the dark room.

SPECIAL PLATES AND EMULSIONS

For the study of certain spectral regions or for special problems involving speed or fine-grain qualities a wide variety of plates are available. The Eastman 33 plates are not light-sensitive above about $550\text{ m}\mu$, and for observations above this limit orthochromatic or panchromatic negatives must be used, with the corresponding change in safelight or

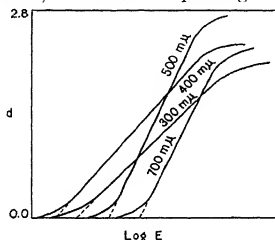


FIG. 13.10.—Variation in chromatic sensitivity for panchromatic emulsion.

complete elimination of a safelight and development in the dark on a time basis. Fig. 13.9 indicates the wedge spectra of some of the common types of Eastman emulsions. In Fig. 13.10 are given the $d/\log I$ curves for a panchromatic emulsion for four wavelength values. It should be noted that the negative indicated in this figure does not have a uniform spectral response, and this should be considered in the application of density calibration patterns on a negative as a means of obtaining relative line intensities in terms of an absolute standard. The theoretically correct application of a calibrated wedge would involve the illumination of the wedge photograph with approximately the same wavelength of light as produces the line which is to be measured. The calibration pattern can be applied in this manner through the use of a Hansen step slit, a gradient or step absorbing wedge, or a rotating sector in front of the slit of the spectrograph. It would be preferable to illuminate the slit with a heterogeneous or continuous spectral source, but a wide slit may be used without much distortion so as to produce a nearly continuous spectrogram from a line source such as an iron arc.

Mees (*C 80*) has recently published (Fig. 13.11) information on a number of special Eastman emulsions which have been prepared for spectro-

POSITIVE AND NEGATIVE REPRODUCTIONS

scopic measurements in the infrared. The sensitivity of these emulsions extends the photographic range to about 1200 or 1300 m μ .

Where high speed of emulsion or certain spectral characteristics are desired one should consult the published data of the Eastman Kodak Company and the Agfa Anseo Corporation (Fig. 13.6). For extremely high speed and fine grain, especial attention is called to the Agfa Ultra

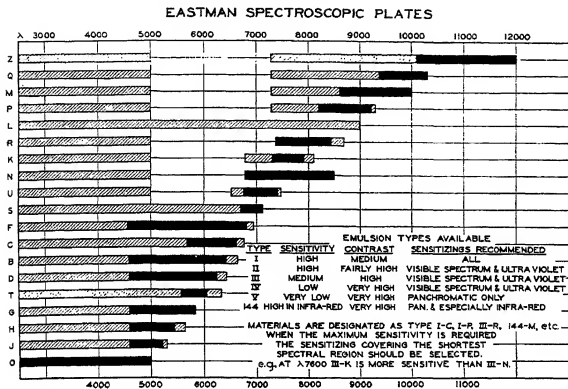


FIG. 13.11.—Eastman spectroscopic plates (C 80).

and Superpan Press films. Most of these special films require time development in total darkness with special developers which are indicated on the package of film.

DIRECT POSITIVE SPECTROGRAMS

As has been pointed out in the introduction (Page 5), there is a lack of agreement among spectroscopists as to the method of presentation of spectrograms in a publication. In many cases the publication of negative (N) spectrograms is avoided because of the necessity of making a negative from the original negative (N) spectrogram and making the positive print from this second negative. Direct positive paper and films are available, and their application to spectrographic work permits the direct preparation of a negative print without going through the intermediate positive reproduction. While the reversal process is quite commonly applied to plates and films, it may also be applied to bromide paper emulsions or special *Direct Positive Paper* (Eastman). The process involves (a) expo-

sure, (b) development of negative, (c) bleaching of negative, (d) clearing, (e) re-exposure, (f) redevelopment, (g) fixing; and after each solution it is necessary to wash the print thoroughly. The entire process can be done in 5 minutes, and except for the care required in giving the correct initial exposure there are no difficult or troublesome steps in the manipulation. Specific directions for developers are usually contained in the packages of special papers prepared for direct positive printing. The papers provided are sufficiently sensitive to use as enlarging papers, and quite satisfactory negative enlargements of negatives can be made by this process.

Special emulsions are available for direct reproduction of negatives in a negative form. Nearly all the amateur motion-picture film is processed by this reversal method so as to provide a positive in place of a negative film. High-speed emulsions are available for this purpose, and it is possible to use them directly in the spectrograph so as to obtain as the original spectrogram a positive rather than a negative, from which direct negative enlargements can be made. Reversible film may also be used in the reproduction of negatives in a negative form as indicated above in the direct positive paper process. More satisfactory results can be obtained in the direct reproduction of negatives as negatives by the use of *Agfa Direct Copy* film. This film has been given a preliminary exposure such that the film if developed directly would give a maximum gamma. As can be seen in Fig. 13.3, the continued exposure of an emulsion will result in a destruction of the latent image. The exposure of this special film in the ordinary printing process results in a destruction of the latent image and by usual developing processes one obtains a negative copy of the negative or a direct copy of the original film.

An advantage of this process over the use of an intermediate positive negative and such film bases as are commonly employed in commercial reproduction lies in the ability of the direct copy film to produce a gamma which is almost identical with the original negative so that relative line intensities will not be appreciably altered by this process.

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CHAPTER XIV

EQUIPMENT AND ARRANGEMENT OF A SPECTROGRAPHIC LABORATORY

CHOICE OF EQUIPMENT

In the organization of a spectrographic laboratory one should be aware of the fact that the expensive spectrographic instruments are usually of such a nature as to be permanent equipment. With careful and proper treatment, spectrographic equipment will outlast the usual life span of the laboratory building or the workers who use it. The initial cost may thus be considered as an investment, with the actual cost of the laboratory figured as the sum of the operation expense and a reasonable amortization of the investment over an extended period of time.

The choice of equipment will naturally depend upon the funds and space available and the use which is to be made of the equipment. Since each will be a special case, one can only advise in a general way with regard to equipment and arrangement. For routine qualitative emission analysis on reasonably large samples the *small* type (Fig. 3.4) should be satisfactory for those elements producing a relatively small number of spectrum lines (tin, lead, silver, zinc, cadmium, magnesium, aluminum, etc.). With an increase in the number of lines, either through the increase in the number of elements or the introduction of elements giving a larger number of lines (such as iron, cobalt, nickel, manganese, molybdenum, platinum, titanium, etc.), one must use higher resolution so as to separate the lines effectively for identification purposes. It is difficult, of course, to set any exact limits to the various instrument types. For example, if the amount of iron present in a zinc alloy is so low that only the persistent lines of iron are present, then high resolution and increased dispersion are not essential. For the analysis of samples containing large amounts of elements producing a complex spectrum the minimum resolution for identification purposes should be equivalent to that obtained on the *medium* spectrograph. For the examination of steels and similar compounds of elements producing complex spectra, an instrument of the *Littrow* type is recommended.

The application of quantitative methods, either densitometer or logarithmic sector, will require about the same resolving power as is necessary

for the qualitative identification. If the amount of material available for examination is small, then high light-gathering power of the spectrograph becomes an important factor. In general, the smaller spectrographs have greater light-gathering power, i.e., the ratio between the focal length and the lens diameter or prism aperture, and it would be a mistake to obtain a large *Littrow* type of spectrograph with the idea that the larger the instrument the more delicate or sensitive would be the photographic response to traces of the unknown. Quartz prism instruments are dependent upon the available supply of natural quartz crystal, which is certainly limited in amount. The difficulty in obtaining highly transparent quartz crystals free from twinning and other defects, and of sufficient size for use, is one of the factors which markedly affects the sale price of the finished instrument.

Improvements in recent years in the ruling of gratings on glass and the application of aluminum reflecting films to such surfaces have increased the accessibility and usefulness of gratings. Although the majority of present-day spectrographic instruments are of a prism type, there can be little doubt that we are passing through the prism era and approaching a grating era. Replica gratings can be produced in plastic material, and for many purposes adequate dispersion and resolution can be obtained from these casts taken from a master ruled grating. The gratings produced by Professor R. W. Wood of Johns Hopkins University are of an unusually high quality, the technique of ruling being developed to such a degree that it has been possible to rule a grating which will concentrate the majority of the spectral reflection in a given order and on a given side of the normal. The accuracy with which new types of organic plastics can be cast into prism, lens, and grating form, without distortion, will undoubtedly open the way for the production of spectrographic instruments, of both prism and grating type, at a considerably lower cost, provided that sales will be sufficient to justify quantity production. Several grating instruments are now available in a convenient laboratory form including original and replica grating dispersion parts (Baird, Hilger, Central Scientific, and Dietert). The optical principle of the grating instrument does not permit the use of a Hartmann diaphragm or logarithmic sector at the slit. The optical system can be altered, however, so as to permit the use of a logarithmic sector or a wedge for superimposed spectrograms.

In the field of absorption spectra analysis, instruments for visual color analysis should be considered separately from ultraviolet equipment. The manually operated types, such as the Bausch and Lomb, Hilger, Gaertner, or König-Martens, are particularly useful for color control and quantitative application to colorimetric reactions. The much

more expensive Hardy-General Electric spectrophotometer is more rapid and accurate than the manually operated types.

Ultraviolet spectrophotometers for the determination of absorption spectra are available from most of the concerns which specialize in spectrographic equipment. Some of these are of a diaphragm type (Hilger-Spekker, Hilger-Judd Lewis, and Kipp and Zonen), some are of a sector type (Bausch and Lomb, Hilger, Zeiss, and Gaertner), and others are of a polarizing type (Bellingham Stanley, Jobin and Yvon, Schmidt and Haensch).

Most of these instruments are designed to be used with spectrographs of the same manufacture although they can usually be adapted to other makes of spectrographs. It is essential in both emission and absorption apparatus that the alignment and adjustment should be simple to maintain and operate, and for this reason most of the instrument-makers are producing instruments with an optical bench for light sources and photometers attached as an integral part of the spectrograph.

No definite recommendations can be made in a general textbook as to any one make or type of instrument since so many factors must influence the choice. The production of properly ground prisms, slits, gratings, and lenses, like that of other fine optical instruments is an art requiring unusual skill, and, hence, the number of producers of satisfactory spectrographic equipment is limited. Nearly all of them maintain a competent staff of technicians to aid and advise with respect to required equipment for a given problem. If one is planning to establish such a laboratory, the advice of research or academic workers connected with universities, government laboratories, or private research and testing laboratories should be sought.

The concerns producing spectrographic equipment for emission and absorption analysis include:

- Adam Hilger, Ltd., London, England (Jarrell-Ash Company, Boston, and A. H. Thomas Company, Philadelphia, American agents).
- Bausch and Lomb Optical Company, Rochester, N. Y.
- Carl Zeiss, Jena, Germany (American office, New York).
- Gaertner Scientific Company, Chicago.
- Jobin and Yvon, Paris, France.
- Franz Schmidt and Haensch, Berlin, Germany.
- Kipp and Zonen, Delft, Holland.
- R. Fuess, Berlin, Germany.
- Bellingham Stanley, London, England.
- Spencer Lens Company, Buffalo.
- Central Scientific Company, Chicago.
- Baird Associates, Cambridge, Mass.
- General Electric Company, Schenectady, N. Y.
- H. W. Dietert Company, Detroit (Applied Research Laboratories).
- C. A. Steinheil Söhne, Munich, Germany.

Suggested equipment and approximate cost:

(a) Rough qualitative measurement of the visual spectrum (direct-vision hand or table spectroscope of either prism or grating type, using a flame, arc, or spark source). Cost, \$5 to \$50.

(b) Accurate visual spectrum measurement (spectrometer with suitable light sources). Cost, \$50 to \$400.

(c) Ultraviolet spectrum photography (small spectrograph and suitable sources). Cost, \$400 to \$700.

(d) Ultraviolet spectrum equipment for quantitative analysis and more accurate qualitative analysis (intermediate type of spectrograph). Cost, \$500 to \$1,200.

(e) Ultraviolet spectrum equipment for quantitative and qualitative of all types of samples excepting those with an extremely large number of lines (medium type of spectrograph with suitable light sources, logarithmic sector, etc.). Cost, \$1,200 to \$2,400.

(f) Ultraviolet spectrum equipment for qualitative and quantitative analysis of substances containing elements producing a large number of lines (Littrow-type spectrograph with suitable light sources, logarithmic sectors, etc.). Cost, \$2,500 to \$5,000.

(g) Rough visual qualitative absorption analysis (hand or table grating or prism spectroscope). Cost, \$5 to \$50.

(h) Accurate visual quantitative absorption analysis (visual spectrophotometer, including spectrometer, photometer, and suitable light sources and cells). Cost, \$1,200 to \$2,500.

(i) Automatic photoelectric measurement of visual absorption spectrum (recording instrument). Cost, \$3,000 to \$6,000.

(j) Minimum equipment for ultraviolet qualitative absorption measurement (small spectrograph with suitable tubes and light sources). Cost, \$400 to \$700.

(k) Minimum equipment for quantitative spectrographic analysis in the ultraviolet (intermediate spectrograph and ultraviolet photometer, cells and light source). Cost, \$1,200 to \$1,600.

(l) Equipment for general quantitative ultraviolet absorption spectrum analysis (medium spectrograph and ultraviolet photometer, cells, and light source). Cost, \$2,000 to \$3,000.

ASSEMBLY AND DESIGN OF LABORATORY

The spectrographic laboratory should be carefully planned so as to be efficiently operated and capable of being kept in continuous operating condition. Such a laboratory is usually a show place in either industrial or research organizations, and some thought should be given to protection of exposed wires and suitable locking nuts or covers for exposed adjustment screws and slit mechanism. If adequate ventilation is provided over arc or spark sources there should be no trouble from fumes, but if the laboratory is subject to fumes the slit mechanism should be protected and the plate holder or a dummy kept in the rack in the instrument. The maintenance of a well-polished laboratory not only creates a good impres-

sion but is essential if accurate analyses are to be made for elemental traces.

The design of modern spectrographs does not require their operation in a dark or poorly lighted room, and except when certain focus adjustments are being made there is no reason why the laboratory should not be reasonably well lighted. For adjustment purposes one may find it convenient, however, to have placed adjacent to each spectrograph a switch to turn on or off the room lights, and some means of reducing the window light should be provided. In the location of spectrographic

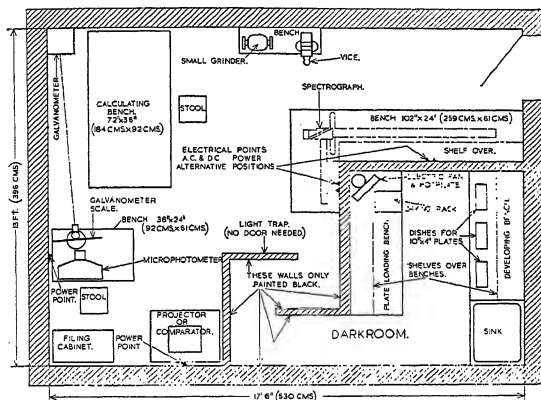


FIG. 14.1.—Plan of a spectrographic laboratory (Hilger).

equipment, one should remember that almost all spectrographs, including both Cornu and Littrow types, are asymmetrical in construction and operate from one side only. One should therefore consult photographs or drawings of the proposed instrument before committing oneself on the laboratory arrangement (Fig. 14.1). Where the analysis equipment involves the photographic process, a dark room should be provided as suggested in Chapter XIII. It is preferable to have a separate room for plate reading, in which suitable tables, charts, plate-reading boxes, and densitometers or projection devices can be operated or used. This same room, which can be darkened, can be easily adapted for visual spectrophotometric equipment.

PERSONNEL

The person in charge of the spectrographic laboratory should have a thorough and intimate knowledge of the operation, adjustment, and calibration of the equipment under his direction. Although a course in spectrographic methods and in theoretical spectroscopy may be of considerable assistance in the solution of problems which are submitted, it is only by continued study and actual laboratory manipulation that one becomes adept at the rapid identification of lines or the matching of beams. A considerable amount of spectrographic analytical work is of a routine character and can be delegated to a laboratory assistant who has not had any special training in this field of analysis. The interpretation of results, however, should be attempted only by those who have a thorough knowledge and appreciation of the significance of the data obtained.

LIBRARY FACILITIES

Spectrographic analysis is largely dependent upon adequate library facilities in the form of comparison negatives of known elements, standard photographic and printed charts (see Chapter IV), a satisfactory set of spectrum-line tables, and a number of standard reference works in spectroscopic and related fields. In general, these tables, charts, and plates form an integral part of the spectrographic laboratory and should be kept in the plate-reading room or spectrographic laboratory rather than in the library of the laboratory or institution. Special mention should be made of the spectrographic publications of the firm of Adam Hilger, Ltd., which has specialized for several generations in the production of spectrographic equipment and the dissemination of information concerning its use and application. Under the guidance of the managing director, Mr. F. Twyman, F.R.S., the company has published spectrum tables, translations of important books on spectroscopy, and numerous original contributions to the field of spectroscopy, and it provides an abstract service on articles of a spectrochemical nature. As has been mentioned elsewhere in this book, it has prepared numerous spectrum charts and has undertaken to produce and dispense special electrodes for control analysis.

The scientific and technical papers from the Bureau of Standards, especially those by Meggers, Kiess, Coblenz, and Gibson; the *Proceedings* of the annual conferences on spectroscopy, held at the Massachusetts Institute of Technology under the direction of Professor G. R. Harrison; and the general reference books and periodicals dealing with spectroscopy should be available in the library of the laboratory or institution.

OPERATION OF THE LABORATORY

The use of the spectrographic equipment should be strictly limited to those workers who have been properly trained and have the permission of the director of the laboratory to make the desired observations. It is desirable to retain in the laboratory all record sheets and plates, both of which should be filed for future reference. A duplicate copy of the data sheet and a print of the negative may be submitted with the analytical report if they are requested. Since special projection devices, viewing boxes, charts and tables are required for the proper interpretation of most analytical spectrograms, it should be quite obvious that the plate records must be kept where they can be easily read or the reported results rechecked if necessary.

Standard data sheets, with serial numbering, should be used for recording spectrograms, and great care should be exercised to see that each negative is numbered to correspond to the data sheet and that the individual spectrograms on the negative are properly recorded on the data sheet. Duplicate analyses should be made whenever possible, and the amount of unknown and exposure so regulated as to insure satisfactory sampling of the material.

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TABLES AND CHARTS

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TABLE I

PERSISTENT LINES BY WAVELENGTH (*Rais Ulines or Letzen Linien*)

After de Gramont-Hartley-Twyman (A71, C63, C40, A36, A22, A50)

1800Å to 8000Å

Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element
'1849.6	Hg I	2404.9	Fe II	2849.7	Ir II	3184.0	V I
54.7	Al III	10.5	Fe II	49.8	Cr II	84.0	V I
56.0	Al II	13.3	Fe II	'52.1	Mg I	'85.4	V I
58.1	Al II	'28.0	Au I	54.6	Pd II	95.0	Cb II
62.5	Al II	37.8	Ag II	55.7	Cr II	'3220.8	Ir I
62.9	Al III	'78.6	C I	60.5	As I	25.5	Cb II
89.9	As I		Pd II	60.9	Cr II	32.5	Sb
1936.9	As I		B I	63.3	Sn I	32.7	Li
42.3	Hg II	'97.7	B I	71.5	Mo II	'47.6	Cu
60.2	Se I	98.8	Pd II	'81.6	Si I	62.3	Os
72.0	As I	2505.7	Pd II	91.0	Mo II	62.3	Sn
'2025.5	Zn II	06.9	Si I	94.9	Lu II	67.5	Sb
39.7	Se I	13.0	Hf II	98.0	Bi I	67.9	Os
61.7	Bi I	16.1	Si I	98.3	Hf I	69.5	Ge I
61.9	Zn II	16.9	'Hf II	2904.4	Hf I	74.0	Cu I
62.1	I I	28.5	Si I	09.1	Mo II	'80.7	Ag I
62.6	Se I	28.5	Sb I	11.4	Lu II	82.3	Zn I
68.4	Sb I	30.7	Te I	16.5	Hf I	89.4	Yb I
'2136.0	Cu II	36.4	P I	24.8	Ir I	90.6	Th II
36.8	P I	36.5	Hg I	29.8	Pt I	3301.6	Os I
'38.5	Zn I	54.0	P I	36.8	Ho II	02.3	Na I
42.8	Te I	'76.1	Mn II	38.3	Bi I	02.6	Zn I
'44.4	Cd II	89.2	W II	40.8	Hf I	02.9	Na I
49.8	P I	93.7	Mn II	45.7	Ru II	'11.1	Ta I
'70.0	Pb I	98.1	Sb I	65.6	Ru II	18.9	Ta I
75.9	Sb I	2605.7	<u>Mn II</u>	76.6	Ru II	21.0	Be I
82.3	Cu II	41.4	Hf II	69.0		21.1	Be I
2203.6	Pb II	51.2	Ge I	98.0		21.4	Be I
46.4	Ag II	51.6	Ge I	3009.1		23.1	Rh I
47.8	Cu II	58.7	Pd II	34.1		45.5	Zn I
'53.9	Ni II	59.4	Pt I	39.1	Ge I	'49.0	Ti II
'64.5	Ni II	76.0	Au I	'64.7	Pt I	61.2	Ti II
65.0	Cd II	78.7	Ru II	'67.7	Bi I	72.8	Ti II
70.2	Ni II	92.1	Ru II	72.9	Hf I	82.9	Ag I
76.6	Bi I	2712.4	Ru II	82.2	Al I	83.8	Ti II
'86.2	Co II	69.7	Te I	92.7	Al I	'92.0	Zr II
'87.1	Ni II	73.4	Hf II	92.9	Al I	96.8	Rh I
'88.0	Cd I	80.2	As I	'93.1	V II	97.0	Lu II
88.1	As I	80.5	Bi I	'94.2	Cb II	3403.7	Cd I
2307.8	Co II	'95.5	Mg II	3102.3	V II	'04.6	Pd I
11.5	Sb I	2802.7	Mg II	10.7	II	06.7	Ta I
'48.6	Be I	09.6	Bi I	18.4	II	'14.8	Ni I
49.8	As I	'16.2	Mo II	25.3	II	21.2	Pd I
78.6	Co II	20.2	Hf II	'30.4	Be II	'34.9	Rh I
'82.0	Fe II	30.3	Pt I	30.8	b II	36.7	Ru I
83.3	Te I	33.1	Pb I	31.1	Be II	37.1	I
85.8	Te I	'35.6	Cr II	34.7	Hf II	38.2	II
88.9	Co II	40.0	Sn I	63.4	b II	52.3	B II
95.6	Fe II	43.3	II	75.1	Sn I	'53.5	Io I
97.1	W II	48.2	Mo II	83.4	V I	65.8	Co I

The most persistent lines are indicated by a prime (') mark.

TABLE I (Continued)

PERSISTENT LINES BY WAVELENGTH

Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element
3466.2	Cd I	3752.5	Os I	4109.9	N I	4730.9	Se I
72.5	Lu II	68.4	Gd I	23.2	La II	39.1	Se I
93.0	Ni I	74.3	Yt II	23.9	Cb I	39.5	Zr I
96.2	Zr II	75.7	Tl I	29.7	Eu II	42.3	Se I
99.0	Ru I	82.2	Os I	37.1	Cb I	72.3	Zr I
99.1	Er I	88.7	Yt II	65.6	Ce II	85.5	Br II
3509.2	Tb I	98.3	Mo I	72.1	Ga I	94.5	Cl I
13.7	Ir I	3814.4	Ra II	77.3	Nd I	4810.0	Cl I
15.1	Ni I	29.4	Mg I	79.4	Pr I	15.6	Zr I
17.0	Pd I	32.3	Mg I	86.6	Ce II	16.7	Br II
19.6	Zr I	38.3	Mg I	89.5	Pr I	25.9	Ra I
24.5	Ni I	48.8	Tb I	4201.8	Rb I	32.1	Sr I
29.8	Co I	64.1	Mo I	05.0	Eu I	61.3	H I
38.8	Th I	74.2	Tb I	15.5	Sr II	72.5	Sr I
47.7	Zr I	88.6	He I	15.6	Rb I	4934.1	Ba II
52.2	U I	91.0	Ho I	25.3	Pr I	62.3	Sr I
54.4	Lu II	3903.0	Mo I	26.6	Ge I	81.7	Ti I
61.8	Tb I	05.5	Si I	26.7	Ca I	91.1	Ti I
72.5	Zr II	06.3	Er I	41.7	U I	99.5	Ti I
96.2	Ru I	07.5	Sc I	54.3	Cr I	5007.2	Ti I
3601.1	Th I	11.8	Sc I	67.0	C II	14.3	Ti I
01.2	Zr I	33.7	Ca II	67.3	C II	5181.2	I I
09.6	Pd I	44.0	Al I	74.8	Cr I	5204.5	Cr I
10.5	Cd I	49.1	La II	89.7	Cr I	06.0	Cr I
13.8	W II	51.2	Nd I	94.6	W I	08.4	Cr I
13.8	Se II	61.5	Al I	4302.1	W I	5350.5	Ti I
30.8	Se II	68.5	Ca II	03.6	Nd I	5400.6	Ne I
34.7	Pd I	88.0	Yb I	90.9	Sa I	24.6	Ba I
35.5	Ti I	4008.8	W I	4424.4	Sa I	55.1	La I
39.6	Pb I	12.4	Ce II	34.3	Sa I	5519.1	Ba I
42.7	Ti I	19.1	Th I	54.8	Ca I	35.5	Ba I
42.8	Se II	30.8	Mn I	55.9	Ca I	70.3	Kr I
46.2	Gd I	33.0	Ga I	56.6	Ca I	5777.7	Ba I
50.2	Hg I	33.1	Mn I	4501.0	Xe I	5832.5	Ne I
53.5	Ti I	34.5	Mn I	11.3	In I	70.9	Kr I
54.8	Hg I	40.8	Ce II	18.5	Lu I	75.6	He I
58.0	Rh I	44.2	K I	24.7	Sn I	90.0	Na I
62.9	Hg I	47.2	K I	54.0	Ba II	95.9	Na I
72.6	U I	57.8	Pb I	55.3	Cs I	5930.6	La I
83.5	Pb I	59.0	Cb I	93.2	Cs I	6249.9	La I
92.4	Rh I	62.9	Pr I	4607.3	Sr I	6402.2	Ne I
92.7	Er I	77.4	La II	24.3	Xe I	6562.8	H I
94.2	Yb I	77.7	Sr II	43.7	Yt I	6707.9	Li I
3710.3	Yt II	79.7	Cb I	71.2	Xe I	6965.4	A I
19.9	Fe I	93.2	Hf I	74.8	Yt I	7067.2	A I
37.1	Fe I	97.3	N III	82.2	Ra II	7503.9	A I
45.6	Fe I	4100.0	N I	85.8	He II	7661.9	K I
45.9	Fe I	01.0	Cb I	87.8	Zr I	99.0	K I
48.2	Ho I	01.8	In I	4704.8	Br II	7800.3	Rb I
48.3	Fe I	03.4	N III	10.1	Zr I	7947.6	Rb I

The most persistent lines are indicated by a prime (') mark.

TABLES AND CHARTS

TABLE II
PERSISTENT LINES BY ELEMENTS
(A71, C63, C40, A36, A22, A40)

1600A to 9000A

Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)
A I	6965.4	Bi I	'3067.7	Cr II	2849.8	Hf II	2641.4
	7067.2	Br II	4704.8		2855.7		2773.4
	7503.9		4785.5		2860.9		2820.2
	8115.3		4816.7	Cs I	4393.2		3134.7
Ag I	'3280.7	C I	'2478.6		4555.3	Hg I	'1849.6
	3382.9	C II	4267.0		'8521.2		2536.5
Ag II	2246.4		4267.3		8943.6		3650.2
	2437.8	Ca I	'4226.7	Cu I	'3247.5		3654.8
Al I	3082.2		4454.8		3274.0		3662.9
	3092.7		4455.9	Cu II	'2136.0	Hg II	1649.8
	3092.9		4456.6		2192.3		1942.3
	3944.0	Ca II	'3933.7		2247.8	Ho I	3748.2
	'3961.5		3968.5	Er I	3499.1		3891.0
Al II	1671.0	Cb I	'4059.0		3692.7	Ho II	2936.8
	1856.0		4079.7		3906.3	I I	1782.9
	1858.1		4101.0	Eu I	4129.7		2062.1
	1862.5		4123.9		4205.0		5161.2
Al III	1854.7		4137.1	Fe I	'3719.9	In I	4101.8
	1862.9	Cb II	'3094.2		3737.1		'4511.3
As I	1889.9		3130.8		3745.6	Ir	2849.7
	1936.9		3163.4		3745.9		2924.8
	1972.0		3195.0		3748.3		'3220.8
	2288.1		3225.5	Fe II	'2382.0		3437.1
	2349.8	Cd I	'2288.0		2395.6		3513.7
	2780.2		3403.7		2404.9	K I	4044.2
	2860.5		3466.2		2410.5		4047.2
Au I	'2427.9		3510.5		2413.3		'7604.9
	2675.9	Cd II	'2144.4	Ga I	4033.0		7699.0
B I	2496.8		2265.0		'4172.0	Kr I	5570.3
	'2497.7	Ce II	4012.4	Gd I	3646.2		5870.9
B II	3452.3		4040.8		3768.4	La I	5455.1
Ba I	5424.6		4165.6	Ge I	2651.2		'5930.6
	5519.1		4186.6		2651.6		6249.9
	'5535.5	Cl I	4794.5		3039.1	La II	'3949.1
	5777.7		4810.0		3269.5		4077.4
Ba II	'4654.0	Co I	'3453.5		4226.6		4123.2
	4934.1		3465.8	H I	4861.3	Li I	3232.7
Be I	'2548.6		3529.8		6562.8		'6707.9
	3321.0	Co II	'2286.2	He I	'3888.6	Lu I	4518.5
	3321.1		2307.8		5875.6	Lu II	2894.9
	3321.4		2378.6	He II	1640.5		3472.5
Be II	'3130.4		2388.0		4665.8		3554.4
	3131.1	Cr I	'4254.3	Hf I	2898.2	Mg I	'2852.1
Bi I	2061.7		4274.8		2904.4		3829.4
	2276.6		4289.7		2916.5		3832.3
	2780.5		5204.5		2940.8		3838.3
	2809.6		5206.0		3072.9	Mg II	'2795.5
	2898.0		5208.4		4093.2		2802.7
	2938.3	Cr II	'2835.6	Hf II	2513.0	Mn I	'4030.8
	2989.0		2843.3		2516.9		4033.1

The most persistent lines are indicated by a prime (') mark.

TABLE II (Continued)

PERSISTENT LINES BY ELEMENTS

Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)	Element	Wavelength (angstroms)
Mn I	4034.5	Pd I	3634.7	Sc I	'3911.8	Ti II	3372.8
Mn II	'2576.1	Pd II	2488.9	Sc II	'3613.8		3383.8
	2593.7		2498.8		3630.8	Ti I	3775.7
	2605.7		2505.7		3642.8		'5350.5
Mo I	'3798.3		2658.7	Se I	1960.2	U I	3552.2
	3864.1		2854.6		'4730.9		3672.6
	3903.0	Pr I	4062.8		4739.1		4241.7
Mo II	'2816.2		4179.4		4742.3	V I	3183.4
	2848.2		4189.5	Si I	2506.9		3184.0
	2871.5		4225.3		2516.1		'3185.4
	2891.0	Pt I	2659.4		2528.5	V II	'3093.1
	2909.1		2830.3		'2881.6		3102.3
N I	'4100.0		2929.8		3095.5		3110.7
N II	5666.6		2998.0	Sn I	2340.0		3118.4
N III	4097.3		'3064.7		2362.3		3125.3
Na I	3302.3	Ra I	'4825.9		3009.1	W I	'4008.8
	3302.9	Ra II	'3814.4		3034.1		4294.6
	'5890.0		4682.2		3175.0		4302.1
	5895.9	Rb I	4201.8		3263.3	W II	2397.1
Nd I	3951.2		4215.6		4524.7		2589.2
	4177.3		'7800.3	Sr I	'4607.3		3613.8
	4303.6		7947.6		4832.1	Xe I	4501.0
Ne I	5400.6	Rh I	3323.1		4872.5		4624.3
	5832.5		'3434.9		4962.3		4671.2
	6402.3		3658.0	Sr II	'4077.7	Y I	4643.7
Ni I	'3414.8		3692.4		4215.5		'4674.8
	3493.0	Ru I	3436.7	Ta I	'3311.1	Yb I	3289.4
	3515.1		'3499.0		3318.9		3694.2
	3524.5		3596.2		3406.7		3988.0
Ni II	2253.9	Ru II	2678.7	Tb I	3509.2	Yt II	'3710.3
	2264.5		2692.1		3561.8		3774.3
	2270.2		2712.4		3848.8		3788.7
	'2287.1		2976.6		3874.2	Zn I	'2138.5
Os I	3262.3	S I	1807.4	Te I	2142.8		3282.3
	3267.9		1820.5		2530.7		3302.6
	3782.2		4696.3		2769.7		3344.5
P I	1774.8		9212.8	Th I	3538.8	Zn II	'2025.5
	2149.8		9228.2		3601.1		2061.9
	2536.4		9237.7		4019.1	Zr I	'3519.6
	2554.0	Sa I	4390.9	Th II	3290.6		3547.7
Pb I	'2170.0		4424.4	Ti I	3635.5		3691.2
	2833.1		4434.3		3642.7		4687.8
	3639.6	Sb I	2068.4		'3653.5		4710.1
	3683.5		2175.9		4981.7		4739.3
	4057.8		2311.5		4991.1		4772.3
Pb II	1682.4		2528.5		4999.5		4815.6
	'2203.6		2598.1		5007.2	Zr II	'3392.0
	'3404.6		3232.5		5014.3		3438.2
Pd I	3517.0		3267.5	Ti II	'3349.0		3496.2
	3609.6	Sc I	3907.5		3361.2		3572.5

The most persistent lines are indicated by a prime (') mark.

TABLE III

PRINCIPAL LINES BY WAVELENGTH

(A41, A10, A59, A23, A36, A27)

Wavelength values are given to unit angstrom values only; those elements with the same unit values are placed on the same line in the order of their occurrence, with a dash (—) to indicate the 0.5 angstrom position. If no dash appears, all the values are greater than 0.5.

To indicate intensity of lines the following notations are used:

Bold face type (Ba) indicates intensity 10 to 8 inclusive.

Normal type (Cs) indicates intensity 7 to 5 inclusive.

Italic type (Sn) indicates intensity 4 to 2 inclusive.

The nonmetals and gases, He, Ne, A, Kr, O, N, Cl, Br, F, S, Se, H, and some of the rarer elements have been omitted from this table. (See Tables V and VI for spark spectra in air and principal lines by discharge spectra.)

For more complete tables see Kayser's "Hauptlinien" (A41) or Harrison's "100,000 line table" (27)

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
2000	Cu—	2110	Bi(R)—	2165	Cu(R)—As Co Fe
20	Fe	11	Pb	66	Ag Fe Fe
23	P I	12	Pb Cu—Ca II	68	Tl I (R)
25	P I—Zn II	13	As—Sn(R) Ag	70	Pb(R)—
28	Mg I—Zn	14	Fe	71	Fe Sn(R)—
32	P I	15	Pb(R)—	75	Pb(R) Sb I (R)
34	P I—	17	Sb—	76	Bi(R)
35	Ca—	20	Ag—	78	Fe—Cu(R)
38	Se—	21	Sn(R)—	79	Sb(R) Cu—
39	Cr—	24	Si I (R)—	81	Cu(R)
40	Se—Ca	26	Cu—	83	As—
44	Au—	27	Sb I	85	Ag
53	Sn	32	Bi(R)	86	Co
54	Hg—	33	As	89	Bi(R) Cu
61	Bi(R) Zn II	34	Bi(R)—	91	Fe
63	Sn Se Fe	35	Cu	92	Cu—
64	Zn II—	36	P I—P I	94	Sn(R)
65	Cr—	37	Sb—	96	Fe—Co
68	Sb(R)—Sn	38	Zn I (R)	97	Ca II
72	Sn(R)	39	Fe Sb	99	Sn(R)—Fe
74	Se	41	Sn(R)—Sb		
75	In—	43	Te(R)—	2200	Cu(R) Fe—Fe Ca I
79	Sb	44	As Cd II (R) Fe—	01	Sb—
80	Sn—	45	Sb—Ag	02	Ag—
81	Te	47	Te—	03	Sb Bi—Pb
84	Fe—	48	Sn(R)	04	Al I (R)
88	Pb(R)—	49	P I	05	As—
91	Sn(R)	51	Sn(R)—Fe	06	As—
93	Fe	52	Bi(R)	07	Tl I (R)—Co
96	Sn(R)—	53	Bi(R) P I	08	Sb Ca II Te
98	Sb—	54	Cr P I	09	Sn(R)
		56	Bi(R)	10	Al I (R) Cu—Tl(R) Si I
2100	Zn II Sn(R)	57	Cr	11	Si I
03	Ca II—	59	Sb—Pb(R) Fe	12	Co—
04	Cu(R)	60	Te—	13	Fe Co
05	Co—	62	Cr	14	Bi—Cu(R) Ba
06	Fe—Co	64	Bi(R) Se—	15	Cu(R)

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
2216	Ba Si I	2292	Fe	2368	Ir—Fe II
20	Sb	93	Sb—Cu (R)	69	Al II—As(R) Cu I
21	Fe—	94	Cu—Cd II	70	Fe As (R)
22	Sb—	96	Pd C	72	Al I Pd—Ir
24	Bi—Hg II Sb	97	Fe I	73	Ba Al I (R) Al I (R)—
25	Cu(R)	98	Fe I—		Fe Sb(R) Fe II
27	Cu(R)			75	Ag—
28	Bi(R)—As Cu	2302	Pd—Ni	76	Au—
29	Fe—Ag	03	Si Cu—	77	Pt—
30	Cu(R)—Bi I (R)	04	Ba II (R)—	78	Hg I Al I—Co
31	Fe—Sn(R)	06	Sb(R)—Cd(R)	79	Fe—Ti I (R)
37	Pb(R)—Ti I (R)	07	Co	80	Sn(R) Fe
38	Cu I (R)—	08	Pt—	81	As I (R)—Ir Dy
39	Cd(R)	09	Bi—Ag(R)	82	Fe II—
40	Fe	10	Fe I—Pt Ni I (R)	83	Fe Te(R) Co—Sb(R)
42	Cu Ir	11	Sb I (R)		Pt
43	Y—	12	Ni I (R)—	84	Mn Ti—
45	Fe Ba	13	Fe I—	85	Y—Te(R)
46	Sn(R) Ag—Zn Pb(R)	16	Ti I (R) Ni—	86	Rh Co—
48	Ag Fe	17	Ag Ni I (R) Sn(R)—	87	Au
49	Fe—	19	Cu	88	Fe Pb(R) Co
51	Sn(R)—Fe	20	Ni I (R) Ag—	89	In I (R) Fe
53	Fe—Pb(R)	21	Mn Ni I (R)—Al II	92	La—Cu
54	Ba	25	Ag—Mn Ni I (R)	93	Zn Pb(R)
55	Te(R) Fe	27	Fe II—	94	Ni
58	Al I—	29	Cd(R)—	95	Sb Fe—Fe II
59	Te(R)—	31	Ag—	97	W—
60	Hg II Cu(R)—Fe	32	Pb(R)—Y Fe II	98	Ca I (R)
62	Hg—Sb	33	Bi	99	In I (R) Fe Hg I
63	Cu(R) Al I (R)—	34	Rh Sn(R)		—Pb(R)
64	Fe—	35	Ba II (R)—		
65	Cd II (R) Fe—Te(R)	38	Fe—	2400	Cu—Ta Bi(R)
66	Fe	40	Pt In I (R)—	01	Pt Pb(R)
67	Fe Sn(R) Cd(R)—Fe	43	Fe II	02	Ru
68	Sn(R)	45	Ni I (R)	03	Pt(R)—
69	Al I (R) Al I (R)—	47	Ba II	04	Fe—Fe II
71	As—	48	Be I (R)	06	Fe Cu
72	Fe	49	As I (R)	07	Co I (R)—Ru
73	Ni	50	Be	08	Sn(R)—
74	Fe—Cs Co	51	Fe Hf—	10	Fe II
75	Ca I (R)	52	Au	11	Fe—Co I (R) Pb(R)
76	Fe I Cu I—Bi I (R) Co	54	Y—Sn(R) Fe	13	Ag Fe—
79	Ni Fe	56	Cu Dy	14	Co I (R)—Pd
80	Fe—	57	Pt(R)—Sn Ag	15	Co I (R)—Rh
82	Sn—	59	Fe—	16	Ni—
83	Au—Co	60	Fe II—Sb	17	Ge—Co
86	Co—Sn(R) Cu	61	Y	18	Pt Ti—Rh
87	Fe—Fe	62	Fe—	20	Y—Rh
88	Cd I (R) As I (R) Pt—	63	Ir—Co	21	Ti—Sn(R)
89	Fe Sb—	64	Au Fe	22	Sb Y—Dy
90	Ni—Fe	66	Fe	24	Ti Pd—Co I (R)
91	Fe—	67	Al I (R)—	25	Li I (R)

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
2426	<i>Sb</i> (R)— <i>Pb</i>	2488	<i>Mn Fe I—Os Pt W Pd</i>	2541	<i>Ti Co</i>
27	<i>Rh W—Au I</i> (R)	89	<i>W Bi—Cu Fe I</i>	42	<i>Zr Fe Zn I—Os Mn</i>
28	<i>Sr I</i> (R)	90	<i>Fe I Rh</i>	43	<i>Ru—Fe Ir</i>
29	<i>Sn</i> (R) <i>Ag</i>	91	<i>Fe I—Zn I</i>	44	<i>Au—Fe Pd Cu</i>
30	<i>Pd</i>	92	<i>Cu</i> (R)—	45	<i>Sc II—Rh Fe I</i>
32	<i>Co I</i> (R)—	93	<i>Zn I Tl I</i> (R)	47	<i>Y</i>
33	<i>Pd Bi—</i>	94	<i>Be—Rh Be</i>	48	<i>Mn</i>
35	<i>Si I</i> (R)—	95	<i>Sn</i> (R) <i>Pt</i>	49	<i>Fe I</i>
36	<i>Pt</i> (R)	96	<i>Fe Pd B</i> (R)	50	<i>Ir</i>
37	<i>Ag Ni</i>	97	<i>B</i> (R) <i>Ge</i>	52	<i>Pt Sc II—Tl I</i> (R)
38	<i>Si Dy</i>	98	<i>Ru—Pt Ru Pd Fe</i>		<i>Tl I</i> (R)
39	<i>Fe Zn I</i>			53	<i>Cd I</i>
40	<i>Pt</i> (R)—	2500	<i>Ga</i> (R)—	54	<i>P I—Sb</i>
41	<i>Pd</i> (R)— <i>Cu</i> (R)	01	<i>Fe I—</i>	55	<i>Rh—P I Sc II</i>
42	<i>Fe</i>	02	<i>Zn II—Ir</i>	56	<i>Mn Mn</i>
43	<i>Si I—Pb</i> (R) <i>Fe</i>	04	<i>Rh—</i>	57	<i>Zn II</i>
44	<i>Rh—</i>	05	<i>Rh—Pd Pt</i>	58	<i>Sn—Rh</i>
45	<i>Sb I</i> (R)	06	<i>Co—Ag Si I</i> (R)	59	<i>Co—</i>
46	<i>Pb</i> (R)— <i>Hg I</i>	07	<i>Ru—Fe</i>	60	<i>In I</i> (R) <i>Dy Sc II—</i>
47	<i>Fe I Ag Pd</i> (R)	08	<i>Pt</i>	62	<i>Li I</i> (R) <i>Fe II</i>
48	<i>Bi—</i>	09	<i>C—</i>	63	<i>Sc II Fe II—Mn</i>
49	<i>Zr</i>	10	<i>Au Rh Fe I Ni</i>	64	<i>Co Ir—</i>
50	<i>Ga</i> (R) <i>Ti—Pt Pt</i>	11	<i>Co</i> (R)—	66	<i>Fe II</i>
52	<i>Mn II</i> (R)	12	<i>C Fe—Ir</i>	67	<i>Rh—Zr Zn I Al II</i> (R)
53	<i>Ag Fe—</i>	14	<i>Si I</i> (R)—	68	<i>Ru Zr</i>
55	<i>Sn—Ru Rh</i>	15	<i>Pt—Pt Bi</i> (R) <i>Zn I</i>	69	<i>W—Sr I</i> (R) <i>Pd Fe Fe</i>
56	<i>Ru—As</i> (R) <i>Ru</i>	16	<i>Si I</i> (R)— <i>Hf</i>		<i>Zn I</i> (R)
57	<i>Zr—Fe Pd</i>	17	<i>Tl I</i> (R)— <i>Fe Co</i> (R)	70	<i>Fe Fe</i>
58	<i>Rh</i>	18	<i>Fe I—</i>	71	<i>Ti Lu Zr W—Sn</i> (R)
60	<i>In I</i> (R) <i>Hf—Y</i>	19	<i>Si I</i> (R)—	72	<i>Mn</i>
61	<i>Rh Os—</i>	20	<i>Rh Ti</i>	73	<i>Cd II—</i>
62	<i>Fe I—Fe I</i>	21	<i>Co I</i> (R) <i>In I</i> (R)—	74	<i>V Sb Fe Co</i> (R)— <i>Co</i>
63	<i>Rh</i>	22	<i>In I</i> (R) <i>Fe</i>	75	<i>Al I</i> (R) <i>Al I</i> (R)— <i>Ag</i>
64	<i>Hg I Co—</i>	23	<i>Fe Sn</i> (R)		<i>Mn Fe</i>
65	<i>Fe—</i>	24	<i>Si I</i> (R) <i>Fe I—Bi</i> (R)	76	<i>Mn II</i> (R) <i>Hg I—Fe Fe</i>
67	<i>Pt</i> (R)—	25	<i>Ti</i>	77	<i>Pb</i> (R)— <i>Fe II</i>
68	<i>In I</i> (R)— <i>Fe</i>	26	<i>V—</i>	78	<i>Lu</i>
72	<i>Fe—Fe I Fe I</i>	27	<i>Mn Fe I—</i>	80	<i>Tl I</i> (R) <i>Co—</i>
73	<i>Fe—Ag</i>	28	<i>Ti—Si I</i> (R) <i>Sb I</i> (R)	82	<i>Fe—Zn I</i> (R) <i>Fe II</i>
74	<i>Sb Fe</i>		<i>Co I</i> (R)	84	<i>Cb Mn—Fe</i>
75	<i>Li I</i> (R) <i>Rh Ir—</i>	29	<i>Fe I—Fe I Ti</i>	85	<i>Tl I</i> (R) <i>Fe II</i>
76	<i>Pb</i> (R) <i>Pd</i> (R)— <i>Fe</i>	30	<i>Te</i>	87	<i>Co—Fe</i>
77	<i>Ag—</i>	31	<i>Sn Ti—</i>	88	<i>Fe—</i>
78	<i>Sb—C II Ru</i>	32	<i>Zr—</i>	89	<i>Zr Ge W—</i>
79	<i>Zn I Fe I</i>	33	<i>Ge—Fe</i>	90	<i>Au—Os</i>
80	<i>Sb—</i>	34	<i>Ti P I Hg I</i> (R)	91	<i>Ru Ru—Fe I Cr</i> (R)
81	<i>Lu Sb</i>	35	<i>Ag—Fe I Ti</i>	92	<i>Ir Mn—Ge Fe Mn</i>
82	<i>Hg I—</i>	36	<i>P I Pt—Hg I</i> (R)	93	<i>Mn II</i> (R) <i>Na I</i> (R)
83	<i>Fe</i> (R) <i>Sn</i> (R)— <i>Fe</i>	37	<i>Fe—</i>		<i>Na I</i> (R)
84	<i>Fe I—</i>	38	<i>Os Tl I</i> (R) <i>Mo—</i>	94	<i>Sn</i> (R)—
86	<i>Fe—Fe</i>	39	<i>Pt—Mn Rh</i>	95	<i>Mn</i>
87	<i>Fe Pt</i> (R) <i>Fe—Rh</i>	40	<i>Hg</i> (R)— <i>Fe I</i>	96	<i>Pt—Ti I Ba I</i>

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
2598	Sb I (R) Fe II—W	2656	Fe V—Ta	2706	Fe V—Sn(R) Fe V Fe
99	Fe II—Fe Ti I	57	Lu	08	Mn—Fe Ra
2600	Dy—	58	W Pt—Os Pd	09	Fe Ti I (R)—Ge
01	In I (R)	59	Pt(R)—Ga	10	In I (R) Mn—Fe
03	Pt Rh—	60	Al(R) Cd I Ag—Mo		Tl I (R)
05	Ti I—Mn II (R)	61	Ru Sn(R) V(R)—Ru	11	Fe Fe
06	Ag Rh—Fe		Ti Ir	12	Ag Cr Ru—Zn I Cd I
07	Fe II—	62	Ir Fe		Ir
08	Ir—Fe Zn I (R) Ti I	63	Pb(R) Cr—Co	13	Pt Mn I—In I (R)
	(R)	64	Fe W—Fe Ru Ir	14	V Fe II—Ta Fe
09	Ru—Ti I (R)	65	Tl I	15	Rh—V Co
10	Mn Lo—Fe I	66	Cr Fe—Fe Fe Fe	16	Fe—
11	Ti I (R) Ti I—Fe II	67	Zr	17	Mo Ru—Fe
12	Sb(R)—Fe	68	Mg I Eu—Cr II	18	Fe—Sb(R)
13	Lu—Rh Pb(R) Fe II	69	W—Fe Ti Mg I	19	Pt(R) Fe Fe—Ru Ga
14	Pb(R)—Ag Fe Sb	70	Zn I Sb I (R)	20	Fe—Fe I
15	Lu—	71	Rh—Cr II Ir Cb	21	Ag Cb
17	Fe II	72	V—Mg I Cr II Mo	22	Zr W Cr
18	Fe Mn Cu(R)—Fe I	73	Cb Ir	23	Y—Fe I
19	Fe Lu—Pt Ti I	74	Pt	24	Fe Fe
20	W Fe II—Fe	75	Au I (R) Co	25	Ru—
21	Fe II	77	Pt(R) Cr(R)—Cd IV	26	Fe Mn I Fe Zr—Cr(R)
22	Rh Hf	78	V Zr Ru Cr	27	Sb(R) Cr Fe—Fe Eu
23	Fe	79	Fe V—Mo Ti	28	Fe—V Fe Fe Rh Lu
25	Rh—Fe Fe II	80	Na I (R) Na I (R) Fe	29	Eu—Pt
			—Rh	30	Bi(R) Fe Fe
27	Pt—Bi(R)	81	Fe	31	Co—Cr(R)
28	Pt(R) Pb(R) Fe II—	82	Sb(R) V	33	Ti—Mg I Fe I Cd I
29	Cd I—Fe I	83	V Mo—		Pt(R)
30	Fe—Zr	84	Mo Zn I—Fe	34	Fe Fe Ru Pt—Mg
31	Fe II Si I Fe—Ti I	85	Ta Co—		Zr
32	Fe Ti I—	86	Ru—Rh Rh	35	Fe I—Fe Ru
34	Ba II Dy	87	Cr—V	36	Cr(R)—Mg I Fe II
35	Ta Ru Fe Pd	88	Cr—Au V Ti	37	Fe I Rh—Fe
36	Fe—	89	Fe—Os Fe V	38	Pt—
37	Os—	90	Fe I V—V	39	Ru Ba Er—Fe II
38	Eu Mo	91	Cr Ge—	40	Ge Co—
39	Pt—Cd I (R) Ir	92	Ru Sb(R) Ir—Fe	41	Li I (R)—Rh
41	Ti I Eu C Ba II—Au	93	Cr Mg I	42	Fe I Cr II Fe I Ti
	Fe—Hf	94	Ir Rh—Fe Co		Fe I—Y Zr
42	Ru Rh	95	Fe Mg I—Fe Co	43	Fe II—Fe Cr II Zr
44	Fe Os Ge Ti I Mo—	96	Fe Ce Fe—Bi(R)	44	Fe I—Fe
45	Pt—	97	Fe Cb—Pb(R) W Cr	45	As I (R) Co—Zr
46	Ta Mo—Ti I Pt(R)	98	Mg I Ta Pt—	46	Fe II—Ni I Fe II
47	Ba II Hf Ta—Fe	99	Fe—	47	C II—Pt
48	Co Ru			48	Au(R) Cr(R)—Cd II
50	Be—Pb Pt(R) Be	2700	Zr—Au V		Ta Cr II
51	Ce Ge—Ge Fe Ru	01	Ru Mo—Mn Lu Eu	49	Fe Fe I Fe—Ta
52	Hg I (R) Al I (R)—	02	V Pt(R)—Ba I Ru	50	Fe I—Cr II Fe
	Sb(R) Rh	03	Rh Mn I	51	Cr II
53	Ta—Cr II Hg I (R)	04	Fe—Os(R)	52	Zr—Ta Ru Hg I
55	Hg I (R)—Mn	05	Rh Hf Mn Pt(R)		Cr(R)

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLES AND CHARTS

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
2753	<i>Fe—Fe Pt In I (R)</i>	2800	<i>Zn I (R)—Zn I (R) Ir</i>	2851	<i>Ti Sb Cr—Mg I V</i>
54	<i>Fe I Lu—Ge Pt</i>	01	<i>Mn I (R)—</i>		<i>Fe</i>
55	<i>Dy Fe II</i>	02	<i>Zn I (R) Pb(R) Ta—</i>	52	<i>Mg I (R) Dy—Na I</i>
56	<i>Fe I Fe I Zn I (R)—</i>		<i>Ti Mg II (R)</i>		<i>V</i>
57	<i>Cr(R) Fe Ti—Cr II</i>	03	<i>Pt—Hg I</i>	53	<i>Na I (R) Pt—Fe</i>
58	<i>Ti Ta—</i>	04	<i>Fe</i>	54	<i>Ru Y—Pd</i>
59	<i>Fe</i>	05	<i>W</i>	55	<i>V—Cr II</i>
60	<i>Y—</i>	06	<i>Os Fe</i>	56	<i>Rh—</i>
61	<i>Co—Fe I Fe</i>	07	<i>Pd Mo</i>	58	<i>Fe—Fe I</i>
62	<i>Fe I—Cr II Fe</i>	08	<i>La Pt—</i>	59	<i>V</i>
63	<i>Pd(R) Fe Ru—</i>	09	<i>Bi(R)</i>	60	<i>Ru As I—Rh Cr Os</i>
	<i>Cd I (R)</i>	10	<i>Ru V Ti—Ru</i>	61	<i>Ru—</i>
64	<i>Cd I (R) Co W Fe—</i>	12	<i>Cr—Sn Mn</i>	62	<i>Cd I Ti—Fe Cr II Rh</i>
66	<i>Co Cu I—Cr II (R)</i>	13	<i>Fe I Mn—Sn(R) Ra</i>	63	<i>Sn(R) Fe—Bi(R) Ir</i>
	<i>Pt Fe I</i>		<i>Eu</i>		<i>Fe I</i>
67	<i>Fe I Rh Ti I (R)</i>	15	<i>Co</i>	64	<i>V—</i>
68	<i>Rh—Cu I Ru W(R)</i>	16	<i>Mo Dy—</i>	65	<i>Fe—Ni I</i>
69	<i>Fe Fe—Te Fe W(R)</i>	17	<i>Fe</i>	66	<i>Hf—V Ru Fe Ir</i>
	<i>Pt Cr(R) Sb I (R)</i>	18	<i>W(R) Pt Ru—</i>		<i>Cr II</i>
70	<i>Zn I (R) W(R)</i>	19	<i>Rh—</i>	67	<i>Cr II</i>
	<i>Zn I (R)</i>	20	<i>Hf—</i>	68	<i>V Cd I—</i>
71	<i>Zn I (R) Ba II—Rh</i>	21	<i>Ni I—</i>	69	<i>Fe I—Zr</i>
	<i>Pt(R)</i>	22	<i>Cr—Mn W</i>	70	<i>Mn Cr II Pt—V</i>
72	<i>Fe Fe I Ir—Dy Pt</i>	23	<i>Ir Pb(R) Fe—</i>	71	<i>Rh—Mo Ru</i>
73	<i>Fe Hf—Pt</i>	24	<i>Cu Ag Ir—</i>	72	<i>Fe—</i>
74	<i>W(R) W(R)—Fe I</i>	25	<i>Fe Fe I</i>	73	<i>Pb(R)—Ag Rh</i>
	<i>Ir Os</i>	26	<i>Ti I (R) Rh—Rh</i>	74	<i>Fe I Ga(R)—Os</i>
75	<i>Cd I In Mo—Ir</i>	27	<i>Rh—Ru Fe I</i>	75	<i>Ru Fe Cb—Ir Zr</i>
76	<i>W Mg I (R)</i>	28	<i>Ti—Fe</i>		<i>Cr II</i>
78	<i>Rh Cr Fe Fe I</i>	29	<i>Ge—</i>	76	<i>Cb</i>
	<i>Mg I (R)—Fe</i>	30	<i>Pt(R) Cr—Mn</i>	77	<i>Fe Ti—Ir Dy</i>
79	<i>Fe—Sn(R) Mg I (R)</i>	31	<i>W—Fe</i>		<i>Sb I (R)</i>
80	<i>Mo As I (R)—Bi(R)</i>	32	<i>Ti Fe—</i>	78	<i>Rh</i>
	<i>Fe Cr(R)</i>	33	<i>Pb(R) Ir Cs—</i>	79	<i>W(R) Cr(R) W(R)</i>
81	<i>Zn I Mg I (R)—Fe I</i>	34	<i>Pt</i>		<i>Ir—</i>
82	<i>Mg I (R)</i>	35	<i>Fe I—Cr II (R) Fe</i>	80	<i>V—Fe Cd I (R)</i>
83	<i>Rh—Fe</i>	36	<i>Mn Ir—Ra C II</i>	81	<i>Cd I (R)—Si I (R)</i>
85	<i>Mo Sn(R) Y Ir</i>		<i>Cd I (R) In</i>	82	<i>Ru Rh—V Ir Cu</i>
	<i>Ba I—</i>	37	<i>Th—C II</i>	83	<i>Cb Au—Fe</i>
87	<i>Ru Sn Fe</i>	38	<i>Fe Os—Os</i>	84	<i>Ti—V</i>
88	<i>Fe—</i>	39	<i>Ir—Sn(R)</i>	85	<i>Lu La—</i>
89	<i>Fe</i>	40	<i>Cr Ir Fe I—</i>	86	<i>Rh Y Co—Ru Mn</i>
90	<i>Mg II</i>	41	<i>Rh Ti</i>	87	<i>Cr(R)—Fe</i>
91	<i>Rh Co—Fe</i>	42	<i>Rh—</i>	88	<i>Pt—</i>
93	<i>Pt—Ge</i>	43	<i>Cr II (R)—Zr Fe Fe</i>	89	<i>Rh Cr II (R)—Mn V</i>
94	<i>Pt(R)—Mn I (R)</i>	44	<i>Rh Os—Zr</i>	91	<i>Mo Ti II—V Ta Au</i>
95	<i>Mg II (R)</i>	45	<i>Fe</i>	92	<i>Mn V Fe—Ru V</i>
96	<i>Rh Lu</i>	46	<i>V Mg I</i>	93	<i>La Pt Cr(R) V—</i>
97	<i>Ir—Fe</i>	47	<i>Lu Hg II</i>		<i>Hg I Pt</i>
98	<i>Mg II Ir Mn I (R)—</i>	48	<i>Mo Mg I—Fe V</i>	94	<i>Mo—Fe Lu</i>
	<i>Ni I Bi</i>	49	<i>Ir Cr II</i>	95	<i>Fe Ti I—</i>
		50	<i>Ta—Sn(R) Os</i>	96	<i>W(R) V W(R) Cu—Ce</i>

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
2897	<i>Ir</i> — <i>Cb</i> <i>Pt</i> <i>Bi</i> (R)	2944	<i>Ga</i> <i>Fe</i> <i>W</i> (R)— <i>V</i> II	2994	<i>Cr</i> (R) <i>Fe</i> I (R)
98	<i>Cr</i> <i>As</i> I (R)		<i>Pt</i>		<i>Ni</i> I (R)— <i>Cb</i> <i>Ca</i>
99	<i>V</i> <i>Cb</i> <i>Fe</i> — <i>V</i>	45	<i>Ti</i> I— <i>Ru</i>		<i>Ru</i>
2900	<i>Lu</i> —	46	<i>W</i> (R) <i>Ir</i> <i>Ru</i>	95	<i>Cr</i> (R)—
01	<i>Fe</i> — <i>Fe</i>	47	<i>W</i> — <i>Fe</i> <i>Fe</i> I	96	<i>Ir</i> <i>Fe</i> — <i>Cr</i> (R) <i>Y</i>
03	<i>Mo</i> <i>V</i> — <i>V</i>	48	<i>Os</i> <i>Ti</i> <i>Dy</i> <i>Y</i> <i>Fe</i> —	97	<i>Ca</i> I <i>Cu</i> — <i>W</i> <i>Pt</i> (R)
04	<i>V</i> — <i>Ir</i>	49	<i>Mn</i> II— <i>Ru</i>	98	<i>Cr</i> (R)
05	<i>Zr</i> — <i>Cr</i> (R) <i>Pt</i> <i>Au</i>	50	<i>Fe</i> — <i>Cb</i>	99	<i>Gd</i> <i>Fe</i> — <i>Fe</i> <i>Ca</i> I
06	<i>V</i> <i>Dy</i> <i>V</i> — <i>Eu</i>	51	<i>Ir</i> — <i>Lu</i>		
07	<i>Mn</i> <i>Ir</i> <i>V</i> II— <i>Fe</i> <i>Pt</i>	52	<i>V</i> II—	3000	<i>Fe</i> — <i>Ti</i> <i>Ca</i> I <i>Cr</i> (R)
08	<i>Cb</i> — <i>V</i> (R) <i>Ta</i>	53	<i>Fe</i> — <i>Fe</i> II <i>Fe</i> I		<i>Fe</i> I
09	<i>Cr</i> (R) <i>Os</i> <i>Mo</i> — <i>Ir</i>	54	<i>Ru</i> —	01	<i>V</i> —
10	<i>V</i> <i>Rh</i> <i>V</i> — <i>Cb</i> <i>Cr</i> (R)	55	<i>V</i>	02	<i>Ir</i> <i>Pt</i> <i>Ni</i> I (R)—
11	<i>V</i> II <i>Cr</i> (R) <i>Lu</i> — <i>Mo</i>		<i>Ti</i> — <i>Ti</i>		<i>Pd</i> (R)
12	<i>Ti</i> <i>Fe</i> I <i>Pt</i> — <i>Rh</i>	57	<i>In</i> I <i>Fe</i> I— <i>V</i> II	03	<i>Fe</i> I— <i>Ni</i> I (R) <i>Ir</i> <i>Zr</i>
13	<i>Zn</i> <i>Sn</i> (R) <i>Pt</i> <i>Au</i>	59	<i>Pt</i> — <i>Fe</i>	04	<i>Rh</i> —
	<i>Cr</i> (R)	60	<i>Eu</i> — <i>Pt</i>	05	<i>Cr</i> (R)—
14	<i>Rh</i> — <i>Mn</i> I <i>V</i>	61	<i>Cu</i> <i>Cd</i> I—	06	<i>Ru</i> <i>Ca</i> I
15	<i>Mg</i>	62	<i>Os</i> <i>Os</i> — <i>Zr</i> <i>V</i> <i>Ir</i>	07	<i>Fe</i> <i>Fe</i> I—
16	<i>Zr</i> <i>Ru</i> <i>Ir</i> —	63	<i>Ta</i> <i>Lu</i> — <i>Au</i>	08	<i>Fe</i> —
17	<i>Os</i> — <i>Os</i>	64	<i>Cu</i> <i>Er</i> — <i>W</i> <i>Y</i>	09	<i>W</i> <i>Fe</i> <i>Sn</i> (R) <i>Ca</i> I—
18	<i>Fe</i> <i>Zr</i> <i>Ti</i> I (R)—	65	<i>Fe</i> <i>Ta</i> <i>Ru</i> <i>Fe</i> I—		<i>Fe</i> I <i>Pd</i>
19	<i>Y</i> <i>Pt</i> — <i>Ru</i> <i>Hf</i> <i>Os</i> <i>V</i>		<i>Ru</i> <i>Ti</i>	10	<i>Gd</i> — <i>Cu</i>
20	<i>V</i> II— <i>Fe</i>	66	<i>Fe</i> I (R)	11	<i>Ta</i> <i>Fe</i> — <i>Zr</i>
21	<i>Pt</i> — <i>Ti</i> I (R)	67	<i>Ti</i> <i>Hg</i> I (R)— <i>Cr</i> (R)	12	<i>Ni</i> I (R)— <i>Ta</i> <i>Hf</i>
22	<i>Pd</i> (R)	68	<i>V</i> — <i>Rh</i> <i>Zr</i>	13	<i>Cr</i> (R) <i>Os</i> <i>V</i> — <i>Co</i> I
23	<i>Rh</i> <i>Fe</i> <i>Mo</i> — <i>V</i> <i>Fe</i>	69	<i>Fe</i> <i>Fe</i> I— <i>Lu</i>		<i>Cr</i> (R)
24	<i>V</i> II— <i>V</i> II <i>Ir</i>	70	<i>Fe</i> I <i>Au</i> — <i>Fe</i> II	14	<i>Cr</i> (R) <i>Cr</i> (R)
25	<i>Ta</i> <i>Fe</i> <i>Hg</i> I— <i>Mn</i> I	71	<i>Cr</i> (R)— <i>Cr</i>	15	<i>Cr</i> (R)— <i>Fe</i>
	<i>Fe</i>	72	<i>Cb</i>	16	<i>V</i> <i>W</i> — <i>Dy</i>
26	<i>Fe</i> II	73	<i>Fe</i> I <i>Fe</i> I <i>Au</i> —	17	<i>Ce</i> <i>Ti</i> <i>Ru</i> <i>Os</i> <i>Co</i> I <i>Ir</i>
27	<i>Zr</i> — <i>Co</i> <i>Cb</i>	74	<i>Cb</i> <i>V</i> — <i>Y</i> <i>Ir</i>		<i>W</i> (R)— <i>Cr</i> (R) <i>Fe</i> I
28	<i>Pt</i> <i>Ti</i> — <i>Mg</i> II	75	<i>V</i> <i>Cr</i> (R)— <i>V</i>		<i>Pt</i>
29	<i>Fe</i> I <i>Fe</i> — <i>Co</i> <i>Hf</i>	76	<i>V</i> — <i>V</i> <i>Ru</i> <i>Ce</i>	18	<i>Os</i> <i>Zn</i> I— <i>Cr</i> (R)
	<i>Pt</i> (R)	77	<i>V</i> <i>Rh</i>		<i>Cr</i> (R) <i>Fe</i> I
30	<i>Mo</i> <i>Os</i> <i>Pt</i> <i>V</i> II	79	<i>Ru</i> <i>Cr</i> <i>W</i> <i>Ru</i>	19	<i>Ni</i> I <i>Ir</i> <i>Sc</i> I—
31	<i>Os</i> — <i>Si</i> I <i>Rh</i>	80	<i>Fe</i> <i>Cd</i> I (R) <i>Ir</i> <i>Cr</i> (R)	20	<i>Ir</i> <i>Fe</i> — <i>Ga</i> <i>Lu</i>
32	<i>Au</i> — <i>In</i> I (R)	81	<i>V</i> <i>Cd</i> I (R) <i>Fe</i> I—		<i>Fe</i> I (R) <i>Cr</i> (R) <i>Pd</i>
33	<i>Mn</i> II— <i>Ti</i> <i>Ta</i>		<i>Ni</i> I <i>Fe</i>	21	<i>Fe</i> I (R)— <i>Hg</i> I (R)
34	<i>Mo</i> <i>V</i> II— <i>Dy</i> <i>Ir</i>	83	<i>Rh</i> <i>Ti</i> — <i>Fe</i> I (R)		<i>Cu</i> <i>Cr</i> (R) <i>Y</i> <i>Pd</i>
	<i>W</i> (R)	84	<i>Ni</i> I <i>Y</i> — <i>Fe</i> II	22	<i>Y</i> — <i>Cu</i>
35	<i>V</i>	85	<i>Cr</i> <i>Zr</i> — <i>Fe</i> II <i>Ir</i>	23	<i>Hg</i> I—
36	<i>Mg</i> II <i>Ir</i> <i>Mg</i> I <i>Fe</i> I		<i>Cr</i> (R) <i>Dy</i> <i>Cr</i> (R)	24	<i>Fe</i> I <i>Cr</i> (R)— <i>W</i>
37	<i>Ti</i> — <i>V</i> <i>Fe</i>	86	<i>Rh</i> <i>Cr</i> (R)— <i>Rh</i>		<i>Bi</i> (R)
38	<i>Bi</i> (R)— <i>Mg</i> I <i>Ag</i> (R)	87	<i>Co</i> I (R) <i>Fe</i> I— <i>Si</i> I	25	<i>Fe</i> <i>Fe</i> I <i>Er</i>
	<i>Pt</i>	88	<i>Cr</i> (R) <i>Ru</i>	26	<i>Fe</i> I—
39	<i>Mn</i> II—	89	<i>Bi</i> I (R) <i>Cr</i> <i>Lu</i> —	27	<i>Gd</i> <i>Pd</i> (R)
40	<i>Ta</i> <i>Mn</i> I— <i>Fe</i>		<i>Co</i> I (R)	28	<i>Zr</i> <i>Rh</i> <i>Cb</i> —
41	<i>Fe</i> I— <i>Cb</i>	90	<i>Cb</i> <i>Fe</i> — <i>As</i> I	29	<i>Cr</i> (R) <i>Au</i> <i>Ir</i> — <i>Zr</i> <i>Ti</i>
42	<i>Mg</i> I <i>V</i> (R)— <i>Pt</i>	91	<i>Fe</i> <i>Cr</i> (R)		<i>Sb</i> I (R)
43	<i>Ir</i> <i>V</i> — <i>Ga</i> <i>Ni</i> I	92	<i>K</i> I (R)— <i>Ni</i> I	30	<i>Fe</i> <i>Cr</i> (R)— <i>Os</i>
		93	<i>Bi</i> I (R)—	31	<i>Fe</i> — <i>Fe</i> I

Intensity (*Ba* 10 to 8; *Cs* 7 to 5; *Su* 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3032	<i>Pd</i> — <i>Ch Sn</i> (R) <i>As</i> I	3076	<i>Bi</i> I <i>Ir Gd</i>	3120	<i>V</i> (R) <i>Cr</i> II <i>Fe</i> — <i>Ir</i>
	<i>Gd</i>	77	<i>Os Ta Os</i> — <i>Lu Os</i>	21	<i>Co</i> I (R) <i>Co</i> I (R) <i>Rh Zr</i>
33	<i>Au Ru</i> — <i>V</i>	78	<i>Fe Ta Fe</i> — <i>Ti</i> II <i>Tb</i>	22	<i>Ir</i> — <i>Er Rh Au</i> (R)
34	<i>Gd Sn</i> (R) <i>Cr</i> (R)	79	<i>Pt Mn</i>	23	<i>Ti</i> — <i>Rh</i>
	<i>Co</i> I— <i>K</i> I (R) <i>Bi</i>	80	<i>Lu</i> — <i>Ni</i> I <i>Hf Cd</i> I	24	<i>Ru</i> — <i>Ge Ta Cr</i> II
35	<i>Zn</i> I (R)	81	<i>Mn Lu</i>	25	<i>V</i> II— <i>Hg</i> I (R) <i>Fe</i> I
36	<i>Cu Pt</i> — <i>Y</i>	82	<i>Gd Al</i> I (R)—		<i>Zr</i> II <i>Ru</i>
37	<i>Cr</i> (R) <i>Fe</i> I— <i>Ni</i> I (R)		<i>Co</i> I (R)	26	<i>Cu Fe V</i> II—
39	<i>Ge</i> (R) <i>Ir In</i> I (R)—	83	<i>Ir</i> — <i>Fe</i> I <i>Rh</i>	27	<i>Cb</i>
40	<i>Fe</i> — <i>Cr</i> (R) <i>Ir Os</i>	84	<i>Pt Ho</i> — <i>Pt</i>	28	<i>Ir</i> — <i>Cu Y</i>
41	<i>Fe Mo Fe</i> I <i>W</i> (R)	85	<i>Ta</i>	29	<i>Zr Fe</i> — <i>Zr</i> II <i>Y</i>
42	<i>Fe</i> I <i>Ta Co</i> I—	86	<i>Ru Ir</i> — <i>Co</i> I (R) <i>Y</i>	30	<i>Ag V</i> II <i>Be</i> II <i>Rh</i>
	<i>Pt</i> (R) <i>Ir Fe</i> I	87	<i>Rh</i> — <i>Mo V</i>		<i>Cb Ti</i>
43	<i>V</i> (R) <i>Mn Dy</i> — <i>V</i> (R)	88	<i>Ir Ti</i> II <i>Tb</i> —	31	<i>Be</i> II <i>Os</i> — <i>Hg</i> I (R)
44	<i>Co</i> I (R)— <i>Mn V</i> (R)	89	<i>Ru Ti</i> — <i>Tb Co</i> I <i>Ru</i>		<i>Hg</i> I (R)
45	<i>Ni</i> I <i>Fe</i> — <i>Ru</i>	91	<i>Mg</i> I (R)— <i>Fe</i> I <i>Y</i>	32	<i>Cr</i> II— <i>Mo</i> I (R) <i>Ru</i>
46	<i>W</i> (R) <i>Pd</i> — <i>Ti Rh</i>	92	<i>Mo</i> — <i>Al</i> I (R) <i>Al</i> I (R)	33	<i>Cd</i> I <i>Ir V</i> II <i>Zr</i> — <i>Nd</i>
47	<i>Ir</i> — <i>Fe</i> I		<i>Nd</i>	34	<i>Ni</i> I (R) <i>Fe</i> I— <i>V</i>
48	<i>V Ru</i> — <i>Ru Ta Co</i> I	93	<i>Mg</i> I (R) <i>V</i> II— <i>Ta</i>	35	<i>Y Dy</i> —
49	<i>Er Ir</i> — <i>Ta W</i> (R)		<i>Cu</i>	36	<i>Sm</i> — <i>V Ru</i>
50	<i>Al</i> II <i>Cr</i> — <i>Ni</i> I (R)	94	<i>Cb</i> —	37	<i>Rh Co</i> I (R)— <i>Rh</i>
	<i>V</i> (R)	95	<i>Zr Ta</i> — <i>Y</i>	38	<i>Zr</i> II
51	<i>Ce</i>	96	<i>Ru Mg</i> I (R)	39	<i>Pt</i> — <i>Tb Co</i> I (R)
53	<i>Fe V</i> — <i>Tb Cr</i> (R)	97	<i>Ni</i> I <i>Ti</i> — <i>Ru</i>	40	<i>Cu Fe</i> — <i>Ru</i>
54	<i>Ni</i> I (R) <i>Mn Er</i> — <i>Al</i>	98	<i>Fe</i> —	41	<i>Dy Er</i> — <i>Ti Pt Sn</i>
	<i>Zr Ru</i>	99	<i>Ag Zr Ru</i> — <i>Fe</i> I <i>Cu</i>	42	<i>Cu Fe</i> — <i>La Pd Fe</i>
55	<i>Fe Pt</i> — <i>Cb</i>		<i>Fe</i> I	43	<i>Ti Fe</i>
56	<i>Ru V</i> (R)— <i>Lu</i>			44	<i>Ru Fe</i> —
57	<i>Al</i> II <i>Fe</i> I— <i>Ni</i> I (R)	3100	<i>Fe</i> I <i>Ir</i> — <i>Gd Fe</i> I <i>Ru</i>	45	<i>Gd Cb Gd</i> — <i>Ni</i> I
58	<i>Ti</i> — <i>Os</i>		<i>Pt</i>	46	<i>Ce</i> — <i>Cu Gd</i>
59	<i>Fe</i> I (R) <i>Ti</i> II— <i>Pt Al</i>	01	<i>Ni</i> I (R) <i>Ni</i> I (R) <i>Gd</i>	47	<i>Tb Co</i> I (R) <i>Cr</i> II—
60	<i>Co V</i> (R)— <i>Fe</i>	02	<i>K</i> I (R) <i>K</i> I (R)		<i>Rh</i>
61	<i>Ir</i> — <i>Co</i> I		<i>V</i> II— <i>Rh Gd Tb</i>	48	<i>Ti Mn</i> I— <i>Tb</i>
62	<i>Mn</i> —	03	<i>Ta Ce</i> — <i>Pt Ti</i>	49	<i>Co</i> I (R)— <i>W</i>
63	<i>Ce Cu</i> — <i>Ta Dy</i>	04	<i>La Rh</i>	50	<i>Rh</i> — <i>Er Ca</i> I
64	<i>Al</i> — <i>Ir Cb Ni</i> I	05	<i>Ti Ni</i> I—	51	<i>V Fe Rh</i> —
	<i>Pt</i> (R) <i>Ru</i>	06	<i>Ti Zr</i>	52	<i>Ti</i> II— <i>Rh Os Co</i>
65	<i>Sc Pd</i> (R)—	08	<i>Th</i> — <i>Cu</i>	53	<i>Fe</i> — <i>Os Ru</i>
66	<i>Mn Al Ti</i> II <i>Ti</i> II	09	<i>Hf Pd Os</i> —	54	<i>Ti</i> II <i>Fe Er</i> — <i>Co Co</i>
	<i>V</i> (R) <i>Fe</i> —	10	<i>Ti Mn V</i> II	55	<i>Ti</i> II <i>Rh</i>
67	<i>Ge V Fe Fe</i> I <i>Rh</i> —	11	<i>Eu</i> — <i>Y</i>	56	<i>Os Fe</i> — <i>Gd Pt</i>
	<i>Bi</i> I (R)	12	<i>Y Mo</i> —	57	<i>Fe</i> — <i>Fe</i>
68	<i>Fe Ru</i> — <i>Gd Ir</i>	13	<i>Co</i> — <i>Er</i>	58	<i>Mo</i> (R)— <i>Co</i> I (R)
69	<i>Tb Ta</i> — <i>V</i>	14	<i>Ir Pd</i> (R) <i>Ni</i> I <i>Y</i> —		<i>Ca</i> II
70	<i>Tb Mn</i> — <i>Er</i>		<i>Ir Rh</i>	59	<i>Ir</i> — <i>Co</i> I (R) <i>Ru</i>
71	<i>Ti</i> — <i>Ba</i> I (R) <i>Pt Co</i> I	15	<i>Ta</i>	60	<i>W</i> — <i>Fe</i>
72	<i>Zn</i> I (R) <i>Ti</i> II	16	<i>Cu</i> — <i>Fe</i> I	61	<i>Mn</i> I <i>Ti</i> II <i>Gd</i> — <i>Ti</i> II
	<i>Co</i> I (R)— <i>Ti</i> II	17	<i>Au</i> — <i>Ti</i>		<i>Fe</i>
73	<i>Mn Ru</i> — <i>Cu V</i> (R)	18	<i>Ru V</i> II (R) <i>Lu</i> — <i>Ho</i>	62	<i>Ti</i> II <i>Dy</i>
74	<i>Os Mg</i> —		<i>Cr</i> II <i>Ru</i>	63	<i>Cb</i> — <i>Pr</i>
75	<i>Pd Ti</i> II <i>V As</i> I	19	<i>Fe As</i> I <i>Ba Tb Ti</i>	64	<i>Zr</i> —
	<i>Nd</i> — <i>Fe</i> I <i>Zn</i> I (R)		<i>Pt Ti</i>	65	<i>Zr</i> — <i>Fe Zr</i> II

Intensity (*Ba* 10 to 8; *Cs* 7 to 5; *Sn* 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3166	<i>Fe</i> — <i>Ho</i>	3215	<i>Ca I Dy Sm—Cb La</i>	3257	<i>Fe</i>
67	<i>Er</i> —	16	<i>Ru Dy Fe Y II Fe</i>	58	<i>Mn—In I (R) Pd (R)</i>
68	<i>Co Pr—Ti II Ru Ir</i>	17	<i>Ti II K I (R) Nd V Fe</i>	59	<i>Pt</i>
69	<i>Co Co Dy</i>		<i>Cr—K I (R) Ni</i>	60	<i>Fe Mn Ru—Cb Co (R)</i>
70	<i>Ta Mo I (R)—</i>	18	<i>Ti II Ir—Sn Tb Pd</i>	61	<i>Cd I (R)—Ti Pt</i>
71	<i>Fe Lu—Ce (R) Ho</i>	19	<i>Co I—Fe Fe Tb</i>	62	<i>Ir Os Sn (R) Pb</i>
72	<i>Fe Pr—</i>	20	<i>Pb Er Ir</i>		<i>Ba I—Er</i>
73	<i>Y—Fe Ho</i>	21	<i>Ce Th—Dy Ni I (R)</i>	63	<i>Rh V Cb—</i>
74	<i>Co</i>	22	<i>Fe—Ba I Ti II</i>	64	<i>Fe Mn Co I</i>
75	<i>Sn (R) Fe—La</i>	23	<i>Ru Er Cu—Ta</i>	65	<i>Au Fe Co (R)—Fe</i>
76	<i>Pb</i>	24	<i>Ti II—Co Cu Mn</i>		<i>La II</i>
77	<i>Ru Co—Ir Dy</i>	25	<i>Ni I (R) Cb—Fe Ca I</i>	66	<i>Cu Ru Ir—</i>
78	<i>Fe Os—Mn I Fe</i>	26	<i>Dy Ru—Co (R)</i>	67	<i>Er Sb I (R)—V Os</i>
79	<i>Ca II Y II—Rh</i>	27	<i>Fe II Fe</i>	68	<i>Ru Fe Cu Pt—</i>
80	<i>Th Fe—Tb Cr Fe I</i>	28	<i>Mn Fe—Ru Ti Zr Fe</i>	69	<i>Dy Os Ge—Sc I</i>
81	<i>Ca II—Cb Fe Er</i>	29	<i>Fe Ti II Ta Ir Fe</i>	71	<i>Fe V Ir—Rh V Ti</i>
82	<i>Fe Co—Zr</i>		<i>Ti II—Ti I (R)</i>		<i>Co (R) Zr</i>
83	<i>V I (R)—Sm V I (R)</i>	30	<i>Fe Fe Pt—Sm Au</i>	72	<i>Ti Zr Ce—</i>
84	<i>Fe I</i>		<i>Mn Ir Er Fe</i>	73	<i>Zr II Ru Sm—Sc I</i>
85	<i>Er V I (R)—Rh</i>	31	<i>Cu—Zr</i>		<i>Cu I (R)</i>
86	<i>Ru Ti I (R)—Fe</i>	32	<i>Ir Er Os Ti II—</i>	74	<i>Tb—Ru Ca I</i>
87	<i>V</i>		<i>Sb I (R) Li I (R)</i>	75	<i>Os Nd—</i>
88	<i>Th Ru Co—V Fe Fe</i>		<i>Ag Ni I (R)</i>	76	<i>V Fe—</i>
89	<i>Rb—Ru</i>	33	<i>Fe Pt—Fe</i>	77	<i>Ir Co—Ru Eu Os</i>
90	<i>V Ti</i>	34	<i>Zr Ce—Ti II (R)</i>	78	<i>Ho Ti—Fe Co Ti Lu</i>
91	<i>Rh Zr Y—Fe Lu Zr</i>		<i>Fe Ni I (R)</i>	79	<i>Ho Zr II Er—Cu V</i>
92	<i>Ti I (R)—Fe</i>	35	<i>Co Cu Dy</i>	80	<i>Er Fe Tb—Rh (R)</i>
93	<i>La II Fe I Fe—Dy</i>	36	<i>Fe I Cb—Ti II Mn</i>		<i>Ag I (R) Y</i>
	<i>Fe Mo I (R)</i>	37	<i>Co I Mn—Rh V Er</i>	81	<i>Tb—Rh Lu Ba I Pt</i>
94	<i>Cu Hf Fe—Au Ce</i>	38	<i>Ru</i>		<i>Ho</i>
	<i>Cb</i>	39	<i>Ti II (R) Fe—Sm Ti</i>	82	<i>Zn I (R) Ti—V Cu</i>
95	<i>Y II</i>	40	<i>Pt Pb Ir Mn—Mn</i>		<i>Fe</i>
96	<i>Ru Fe</i>	41	<i>Zr Ru—Ir Ti II (R)</i>	83	<i>Tb V Co (R) Cb—</i>
97	<i>Cr Rh Ni I—</i>	42	<i>Ta Y II—Pd (R)</i>		<i>Rh (R) Co</i>
98	<i>V (R) Lu—Ir</i>	43	<i>Ni I (R) Cu—Mn</i>	84	<i>Fe Zr Ru</i>
99	<i>Fe I Tb Ti I (R)</i>		<i>Co (R)</i>	85	<i>Tb Nd Ce Fe—</i>
		44	<i>Fe</i>	86	<i>Ca I Er—Fe Er Ni I</i>
3200	<i>Y II Fe—Er Pt</i>	45	<i>La—</i>	87	<i>Co Pd—Ir Ti Fe Er</i>
01	<i>Ce</i>	46	<i>Fe</i>	89	<i>Mo Rh Er Ho—Rh</i>
02	<i>V (R)—Ti Fe</i>	47	<i>Co (R) Fe—Cu I (R)</i>	90	<i>Pt—Cu Fe Mo Fe</i>
03	<i>Y II—Ti</i>	48	<i>Fe—Mn Ti</i>	92	<i>Fe Ti—Fe</i>
04	<i>Pt—Au</i>	49	<i>Er La—Co I</i>	93	<i>Tb—Cu (R)</i>
05	<i>Ir Er Fe—V</i>	50	<i>Pt—Fe Ni I V</i>	94	<i>Tb Ru Rh</i>
06	<i>Cb—</i>	51	<i>Fe Dy—Pd (R) V Ti</i>	96	<i>Ru—Rh</i>
07	<i>V—</i>		<i>II Pt</i>	98	<i>Sm Fe—Co Cd</i>
08	<i>Er Cu Fe—Dy Mo</i>	52	<i>Y—Cd I Ti II Fe Mn</i>		
09	<i>Cr Fe—Sn I</i>	53	<i>Fe Hf</i>	3300	<i>Nd Rh—</i>
10	<i>Co Er—Fe</i>	54	<i>Cb Co (R) Ti II Lu</i>	01	<i>Os Ru Sr I Pt</i>
11	<i>Fe—Fe</i>		<i>Fe Sm Ir—Ru Ru</i>	02	<i>Pd (R) Na I (R)—</i>
12	<i>Fe V Fe—Eu Mn</i>	55	<i>Pt</i>		<i>Zn I (R) Na I (R)</i>
13	<i>Fe II Ni—Ir</i>	56	<i>In I (R) Mn Mo</i>	03	<i>Zn I (R) La II—Er</i>
14	<i>Fe Zr Ti Rh Er—Ti</i>		<i>Er—Os</i>	05	<i>Zr Dy—Fe</i>

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3306	Ru Zr II Fe Sm—	3350	Ca I Pr Gd—	3386	Nd—
07	Sm Co Fe—Sr I Cu		Rb I (R)	87	Fe—Ti II Os Zr
08	Au—Ti II Dy	51	Sr I (R)—Ta Fe Fe	88	Nd Co I (R) Zr—Y
09	Ti	52	Dy	89	Er Fe
10	Fe—Fe Ir	53	Dy Sc	90	Hg Co—
11	Ta—	54	Fe Co I (R) Zr Cu—	91	Ni I (R)—Lu Zr II
12	Lu Ir Co Er—Dy		Y Ti I	92	Er Th Fe—Ru Fe
	Nd	55	Fe—Pr		Ni I (R)
13	Mn—Mn	56	Zr Fe Co—Sm Ba I	93	Zr—Tb Dy
14	Pr Mn Ti—Zr Fe	57	Zr II—	94	Ti II Fe Pr
15	Pt—Ni I (R)	58	Mo I Ti Cb—Cr II	95	Co I (R)—
16	Mn Ru Er—Ir		Ta Gd Y	96	Zr—Pd Rh(R) Er
17	Dy Fe Cu Mn—Ru	59	Ru Dy Fe I—Lu		Fe I
	Ta		Sc II Ir Rh	97	Lu Y Bi I (R)—
18	Ti II—Ru Ta	60	Cr—Rh Ir	98	Ta—Ho
19	Zr Co Co—Cu Co	61	Ti II (R) Sc II Mo—	99	Fe Zr II—Rh Hf Gd
	Dy		Ni I (R) Ta Ca I		
20	Au Ni I (R)—Mn Ba		Sc II Y	3401	Fe I Ru Ir Er Os Pt
21	Be I Be I—V Ti	62	Ru Rh Gd—	02	Cu Fe Ti—Os
22	Co Sr I Ni I—Fe Ir	63	Mo	03	Cr—Cd I (R) Zr
	Ir Ti II (R)	64	Y	04	Fe—Pd Cu Zr II
23	Zr Rh(R) Er—Fe Pt	65	Cu—V Ni I (R) Sm	05	Co I (R) Bi—Mo I
24	Tb—Fe	66	Ni I (R) Sr I—Ce Er	06	Rh Ta Fe Mo Ta
25	Ru Co Fe—Mo		Fe Fe	07	Dy Fe—Gd Dy
26	Ti II Zr Co	67	Pt Co I (R)—	08	Ir Dy Pt—Sm Cr
27	Mo I—Y	68	Cr II Er Rh Ru—Ir	09	Co I (R) Ru—Ni I
28	Nd—Fe		Sc II	10	Nd Zr II Ho—Ho
29	Ti II (R)—Cu Mg I	69	Ni I (R)	11	Ru
30	Sr—Sn(R) Mn	70	Ti I (R)—Er Os Fe	12	Rh Co I (R) Y—
31	Rh Rh Gd—	71	Ir Ti I (R)—Ta Dy		Co I (R)
32	Ti Mg I—Hf		Ru Ni I (R)	13	Fe Ni I (R)—Tb Dy
34	Co I (R) Ir Zr Eu—Zr	72	Fe Sc II Rh—Tb Er		Ni I (R)
35	Ti II Cu—Ru Fe		Ti II Ho	14	Zr Ni I (R) Ho
36	Os Gd Fe Cr II—	73	Pd(R) Co Zr—	15	Fe Cu
	Mg I	74	Er Ni I (R) Co—Ni	16	Ho—Gd
37	La II—Fe Ru Cu		Ru Zr	17	Dy Co I (R) Ru (R)—
38	Zr—Rh Fe Ho	76	Er La—Lu Ba I	18	Dy—Fe Mo I Gd
39	Tb Fe—Ru Co Cr II	77	Co(R) Dy Rh Ba I—	19	Ir—Dy Pd Ta
40	Mo Ti II Y—Zr Fe		Ti I V Rh Y	20	Rh Tb Ba I—
41	Dy Hg I—Ru	78	Ru—Fe	21	Ba I Ba I Cr
	Ti I (R) Fe Cb	79	Fe Ti—Ru Cr Mo I		Pd(R)—Ho
42	Fe Fe—Cr II Co Rh	80	Fe Ru Ti II—	22	Gd—Fe Cr
43	W—Ho Cb Ti II Pt		Ni I (R) Pd Sr II	23	Ni I (R) Gd
44	Rh Ca I—La II Mo I		Ni I (R) La II	24	Fe Rh—Gd Ir
	Ce Zr	81	Cu Rh Co—	25	Fe Dy Ho Cb—
45	Zn I (R)—Zn I (R)	82	Sm Fe—Mo I Cr	26	Ce Fe I—Cb Fe
	Zn I	83	Sb I—Fe Ti II (R)	27	Fe—Pt
46	Cr(R) Ti II Co		Ag I (R) Fe	28	Ho Ru (R) Fe Co—
47	Mo I—Cr II Fe	84	Os—Mo	29	Ho Dy—Ru
48	Rb I (R) Ti II	85	Dy Ho Er Ru	30	Zr II Ru Ta
49	Ti II (R) Cb Cu		Co I (R)—Lu Rh	31	Co I (R)
	Ti II (R) Tb Cb—		Ti I (R)	32	Cb Ru

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3433	Gd Co I (R) Pd(R)— N I (R) Cr(R)	3475	Fe I (R)—Fe Cu Co(R)—Fe I Ce	3515	Ni I (R)—Ho Ir
34	Mo—Mo I Rh(R)	76	Ti II—	16	Fe—Pd(R)
35	Ru—	77	Cb Rh(R)	17	Dy V Ce—
36	Ta Cr—Ru(R)	78	Zr Hf Zr—Cb	18	Er Co I (R)—
37	Ir Zr Mo Ni I (R)—Ir	79	Er—Ta Al Ti	19	Ti I (R)—Zr Ru Dy
38	Zr II Fe Ru—Mn	80	Zr Pd(R) Ru Gd— Gd	20	Tb Ni I Ho
39	Gd—	81	Gd Mn II	21	Cu Er Co I (R) Ru Ho Ti—
40	Gd Ru—Rh Fe I (R) Dy Fe I (R)	82	Fe I Co I (R) Pt— Zr Cu Ni I (R)	22	Eu Dy Fe I— Co I (R)
41	Er Pd(R) Cr—Mn II	83	Rh Y—Ir Dy Ho	23	Ir—
42	Fe Ce—Co I (R)	84	Ce Pt Fe Co—Y Ni V	24	Co I (R)—Os Tb Co
43	Co I (R) Fe I (R)	85	Er	25	Dy Fe Cu Gd Fe— Ni I (R) Mo V
44	Ti II—	86	Ca I	26	Ba I—Tb Zr
45	Fe—Dy Cr	87	Ce Mn II	27	Fe I Fe Fe—Fe
46	Ni I (R) Ir K I (R) Tb—Dy	88	Er Co I (R)—Ho Fe Pd(R)	28	Co I (R) Dy
47	Mo Os Fe Zr K I (R)—Rh	89	Fe I (R) Co I (R)	29	Cu—Fe Ni I
48	Y Ru Ir	90	Cb Co I (R)—Gd	30	Rh(R)—Gd Os Ru Th
49	Mo Co I (R) Os Co I (R)—Dy	91	Er Ni I (R)	31	Dy Co I (R) Ti I (R)
50	Rh Cu Fe Gd—Y	92	Ho—	32	Ba—V Co I (R) Fe
51	Fe	93	Gd Dy—Ho	33	Fe Cu—V
52	La Fe I—Ni I (R)	94	Fe—Co I (R) Mn II	34	Ru—Ta Dy Ho
53	Er Ho La Cr— Co I (R)	95	Y Zr II—Co I (R) V	35	Mn I (R) Mn I (R)
54	Tb Dy—Cu	96	Fe—Mn II Dy Fe I Ta	36	Mn I (R)—Ru Os
55	Rh Co I (R)—Cr	97	Cb Rh Ho Ru (R)	37	Fe Fe Co I (R)—V Cu
56	Ho Mo I Ti—Zr Dy Ru	98	Ho Er—Cd I	38	Dy
57	Tb Rh Fe V—Zr Tb Cu Rh	99	Tb—Tb Ni I	39	Cb Ti—Sc
58	Fe Ni I (R) Ta—Zr	01	Ba I (R) Os—Ag Ni	40	Dy—Fe
59	Fe	02	Co I (R)—Rh(R)	41	Cb Fe Fe Ru
60	Mn II—Pd(R)	03	Ta	42	Rh—Dy
61	Co—Ti II Ni I (R) Ho	04	Mo V—Sb I Dy Os Ti II Ta	43	Ce—
62	Rh(R) Er—Er Co I (R)	05	Er Hf Rh Dy Zr— Gd Zr Er Dy	44	Fe Tb—
63	Zr Ru—Ta Dy	06	Co I (R)—Fe Dy Ho	45	Fe—Rh
64	Sr II—Er	07	Rh(R) Lu Tb—	46	Fe Eu Dy—Ag Zr Os
65	Ir—Co I (R) Fe I (R)	08	Mo Er Lu Fe—W	47	Co Nd—Fe Rh
66	Cd I (R)—Mo I	09	Tb—Co I (R)	48	Cb Y Dy—Cb Ba I Y Lu
67	Gd—Ni I Cd I (R) Y	10	Tb Cb Ni I (R) Co I (R)—Ti II Bi I (R)	49	V W—Fe Gd
68	Tb Dy Ca I—Fe Gd	11	Ta Eu Y—Th	50	Ho—Tb Dy
69	Er Ni I—Rh Er Th	12	Cu I—Dy Co I (R)	51	Ti—Zr Ba I
70	Rh(R)	13	Er Y	52	Mn I (R)
71	Zr Fe Fe Co—Er	14	Os Co I (R)—Ir Fe I Ni I	53	Mn I (R) Ni I
72	Rh Lu—Ni I (R) Tb		La Ru—Pt Er	54	Mn I (R) Co Y
73	Ru			55	W Gd—Rh Fe
74	Co I (R) Mn II— Mn II Rh(R) Ca I Sr II			56	Dy Cb—Co I (R) Cr
				57	Ni I Dy Zr
				58	Y I Fe Co
				59	Pd(R)—Au Fe
				60	Fe I Lu—Cb Fe

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3556	Zr II Ho I' Fe	3597	Rh(R)—Ni I (R)	3635	Mo Mo Ti I (R)—Cu
57	Gd Ir—	98	Nd Os—Ho Zr	36	Ir Lu—Cr(R) Ba
58	Dy—Fe I Sc II Co I	99	Cu Ba I—Er Fe Ru	37	Ru—Sb I Fe
59	Ir—Os		Er Zr	38	Fe Ho Tb—Er Pt
60	Ce Os Co I (R)			39	Y Co—Rh Pb(R)
61	Hf Tb Ba	3600	Dy—Y II Er Ho Gd		Cr(R)
63	Dy—Cb Dy	01	Th Zr Ir—Y II	40	Dy Os Fe Ba—Ru
64	Rh—Co I (R)	02	Cu Co I (R) Ni I—Cb	41	Er Ti II W—La Tb
65	Fe I (R)—Fe	03	Fe Eu—Cr Fe		Cr
66	Zr V Ni I (R)—U	04	Sm—	42	Ta—Ti I (R) Sc II
	Ba Ta	05	Cr I (R) Co I (R)	43	Pt Co—Dy
67	Fe—Sc II Lu		Fe—Ir Rh	44	Hf Ca I—Ca I
68	Sm—Tb Fe	06	Fe Er	45	Cu Sc II Sm Tb Dy
69	Co I (R) Mn I (R)—	07	Zr Ta—Mn I		La—W Pr Fe
	Mn I (R)	08	Fe Mn I—Fe I (R)	46	Gd Pr—W Er
70	Mn I (R) Fe I (R)	09	Ni I Th Sm—Pd(R)	47	Fe I—Co I (R) Tb Lu
	Fe—Ru W		Nd Ir		Fe I (R)
71	Pd (R) Y—Ni I (R) Fe	10	Ti Fe Mn I Ni I	48	Dy
72	W Zr II—Sc II		Co(R)—Cd I (R)	49	Fe Co—Fe I Ra II
	Pb(R)		Gd	50	Fe Hg I (R) La Fe
73	Ho—Ir Fe Fe	11	Ba Y II Tb—Cs I		Er Tb—
74	La—Co I (R)		Co Zr	51	Cb Fe—Sc II Os
75	Fe Co I (R) Fe—Cb	12	Fe Rh(R)—Ni I	52	Co I (R)
76	Ba Dy Sc II—Fe		Cd I (R)	53	Nd Ti I (R)—Cr
	Zr II Dy	13	Zr Gd—Cu Ce(R)	54	Ru Os—Gd Hg I (R)
77	Ce—Ba Mn I (R) Dy		W Sc II		Tb Rh
78	Y—Cr I (R)	14	Mo Cd I—Zr II Rh	55	Fe—Sm Ce
79	Tb—Ba I	15	Tb	56	Gd Cr—Os
80	Cb—Sc II	16	Fe Er Os	57	W Rh(R)
81	Fe I (R)—Gd	17	Th Ir Fe—W(R) Fe	58	Ti I—Tb
82	Fe—		Er	59	Mo—Th Fe Cb Ti
83	Rh(R)—	18	Fe—Fe I (R)	60	Cb—
84	Dy—Y Fe Co I Fe Gd	19	Ru Ni I—	61	Ru(R) Sm—Ir Rh
85	Dy Co I (R) Fe I—	20	Rh—Y I	62	Co Ti Ho—Ba Hg I
	Fe I	21	Cu Sm Fe—	63	Pt Tb Hg I (R) Gd
86	Fe Ta—Ba Mn I	22	Fe—		Ru—V Zr
	Fe I	23	Fe—Mn I Ce Ir Lu	64	Ni I—Y Ir Gd Cb
87	Rb I (R) Co I (R)	24	Ca I (R) Cu Mo—	65	Nd—
	Nd—Y Ni I		Ni I Ti II Co I	66	Rh—Rh
88	Ba—Fe	25	Fe Ru—Tb	67	Fe—V Ho
89	Cb Fe I Cb Fe—	26	Ir Ru—Rh(R) Ta Ho	68	Zr Y—Pr Ti I
	Sc II V	27	Ho Cu—Rh	69	Er Fe—Fe Ru
90	Sc II		Co I (R) Er	70	U Fe Ni I—Sm Os
91	Dy—Rb I (R) Dy	28	Pt Tb—Ir Y La	71	V Gd Zr—Pb(R)
92	V Dy W—Nd Sm	29	Dy—Mn I		Ti I
	Gd Y I	30	Zr Dy Fe—Ba Ca I	72	Pt Dy Nd—
93	Ru(R) V Cr I (R)—		Sc II Ca I Pr	73	Dy V—Nd
	Cb	31	Fe Sm Co I Fe I (R)—	74	Pt Gd Ni I—Zr II
94	Ir—Fe Co I (R)	32	Fe—Fe Co		Rh Ho
95	Mn I—Er	33	Y Zr—Er Fe	75	Ir—V I
96	Rh Ti Bi (R) Ru(R)	34	Dy Sm Fe—Pd(R)	76	Fe Tb—Co Dy
	Rh (R) Tb		Co Ru(R)	77	Fe

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3678	<i>Ru—Zr</i>	3722	Ni I—Fe I (R)	3768	<i>Er Cr Gd—Er</i>
79	<i>Ce—Th Fe I</i>	23	Sb I	69	Rh
80	<i>Hg I V—Mo</i>	24	Fe Dy—Ti Y Sm <i>Er</i>	70	Mo I <i>Gd I' II</i>
81	Rh—		Eu	71	<i>Er—Ti I Cu Mo</i>
82	Hf Fe <i>Ag I—Pt</i>	25	Ti I <i>Gd—</i>	74	Y II—
83	Co <i>Fe I V I Pb(R)—</i>	26	<i>Ru Cb—Fe Ru(R)</i>	75	Nd—Ni I Ti I (R)
84	<i>Fe Gd Lu Co—Cu</i>	27	V II—Fe I (R) <i>Zr</i>	76	Tb Y Os
85	<i>Ho Ti II (R)—</i>	28	<i>Ru(R) Sm—</i>	78	Rh—V I
86	<i>Fe Gd—</i>	29	<i>Cd I—Ti I (R)</i>	80	Nd—Zr
87	<i>Pr Pr Pt Fe I (R)</i>	30	<i>Fe Ru(R) Co—Gd</i>	81	Cb <i>Er Cb—Mo I</i>
	V—Gd <i>Cb</i>	31	<i>Zr Sm Ir—Mn</i>	82	Os <i>Gd—</i>
88	V I <i>Eu—Ba I</i>	32	Gd Co <i>Fe—V</i>	83	Ni I
89	Os <i>Fe—</i>	33	Gd <i>Fe I (R)—Co</i>	84	Ta Nd—
90	V I <i>Pd(R)—Rh(R)</i>	34	Co <i>Pr—Ir Fe I (R)</i>	85	<i>Er—Fe</i>
	<i>Co</i>	35	Rh <i>Fe—Nd Co Sm</i>	86	<i>Ru(R) Dy Mo—Ce</i>
91	Tb—	36	Ni I Ca II		<i>Fe I Er</i>
92	V I <i>Rh(R)—Y Ho</i>	37	<i>Fe I (R) Rh—</i>	87	Cb V <i>Tb—Er Fe I (R)</i>
	<i>Mo</i>	38	<i>Er Fe—Y</i>	88	<i>DyRh—Y II</i>
93	Co <i>Co—Mn Sm</i>	39	<i>Sm Pr Ru—Cb</i>	90	<i>Fe I Os Cb Mn</i>
94	<i>Fe Ho Er—Tb Dy</i>		<i>Pb(R) Zn</i>		V I— <i>Ru(R) La</i>
	<i>Mo</i>	40	Cb	91	<i>Gd Cb—Er</i>
95	<i>Fe V—Rh V I</i>	41	Ti I Th <i>Cu Sm—</i>	92	Er
96	<i>Er—Ru</i>		Ti II	93	<i>Rh(R) Rh(R)—Ni I</i>
97	Zr II—Gd Cb	42	<i>Ru(R) Mo Cb—Er</i>		Os
98	<i>Dy Zr Rh—Rh</i>		Ru	94	<i>Fe Cb—Li I Ba La</i>
99	<i>Gd Pt</i>	43	<i>Fe—Cr(R) Sm Cr(R)</i>	95	<i>Fe I—Er</i>
		44	<i>Er Rh—</i>	96	<i>Gd Zr—Ho</i>
3700	Co— <i>Cu Rh(R)</i>	45	<i>Er—Co I (R)</i>	97	<i>Er—Fe Cr Sm</i>
01	<i>Fe—Dy</i>		Fe I (R) <i>Sn I'</i>	98	Cb <i>Pd(R) Mo I (R)—</i>
02	Co <i>Ho—Mo Tb</i>		Fe I		Fe I <i>Ru(R) V</i>
03	Os—V I Tb	46	Os—	99	<i>Pd(R) Rh(R) Ru(R)—</i>
04	Co I (R) <i>Fe—V I</i>	47	<i>Ir—Y Dy</i>		Fe I
05	V I—Fe I (R) <i>La II</i>	48	<i>Ti Ho Rh Fe I—Fe</i>		
	<i>Sr I</i>	49	<i>Cr(R) Fe I (R)—Co</i>	3800	Ir Pr <i>Cu—</i>
06	Ca II <i>Ti—Pt</i>	50	<i>Er V II</i>	01	<i>Sn(R) Gd—Ce</i>
07	<i>Fe—Fe I W Fe</i>	51	Zr Co <i>Hg</i>	02	Cb
08	Os	52	Th Os Ti I	03	<i>Er V I—Cb</i>
09	Os <i>Fe I Zr—Ce</i>	53	<i>Ru Fe I Ti I Ho</i>	04	Cb Pr <i>Cr</i>
10	Y II—	54	Rh Rh—	05	<i>Cu Fe—Rh</i>
11	Tb	55	Tb Co(R)—Ru	06	<i>Dy—Fe Rh Tb Mn I</i>
12	<i>Er—Gd Cr</i>	56	<i>Fe</i>	07	Ni I <i>Sr I—Fe</i>
13	<i>Rh(R) Cb—La</i>	57	<i>Ho Dy Tb—Ti II</i>	08	<i>Er Co I—V I</i>
14	Zr <i>Rh La II</i>	58	<i>Fe I (R) Gd—</i>	09	<i>Ce—Mn I</i>
15	V—La	59	<i>La Ti II—Cu Cb</i>	10	Cb—Ho
16	Ce Gd <i>Fe—</i>	60	<i>Ru Fe—Fe</i>	12	<i>Ho V I Co—Fe I</i>
17	Cb Ti I—	61	Ti II — <i>Ru</i>	13	Gd
18	<i>Y—Li Sm Pd(R)</i>	62	<i>Pr—Th</i>	14	<i>Ra II—</i>
	<i>Mn</i>	63	<i>Fe I (R)</i>	15	<i>Rh Cr—V Fe I (R)</i>
19	<i>Li Hf Ru Gd—Os</i>	64	Ce Zr—	16	Cb Co Rh <i>Co—Gd</i>
	Fe I (R)	65	<i>Rh(R) Tb—Fe</i>		Dy Co
20	Os— <i>Cu</i>	66	<i>Er—Zr II</i>	17	<i>Ru—Zr</i>
21	Ti II <i>Th</i>	67	Fe I (R) <i>Ru—</i>	18	V I Pr <i>I'—Pt</i>

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3819	Cb—Cr Eu(R)	3872	Fe I	3916	La Cr I (R) V—Gd Fe
20	Fe I (R)—Er Cu	73	Co I (R)—Fe Co I (R)	17	Co Fe I—
21	Fe—	74	Tb—	18	Hf Mn Er—Ta Fe Pr
22	VI Rh(R)—VI	75	Ce(R) VI (R) Ti—Ca I Nd V	19	Cr I (R)—Tb
23	Mn I (R) Mn I	76	C V—Cs I Lu Os Co I (R)	20	Cb Fe I—Ru Nd
24	Fe I (R)—	77	Pr Rh—	21	Cr I (R)—La II Zr Co
25	Cu I—Fe I (R)	78	Fe I (R) Ce—Fe I (R) Fe	22	Rh Sm V—Co I Fe I (R) Pt
26	Mo I	81	W—Co I (R) Co (R)	23	Gd Ru—
27	Fe I (R)	82	Ti Ti—Ti	24	Ti I
28	Er Rh(R)—V I Mo I	83	Cr I (R)—	25	Pt Tb Pr—Ru Fe
29	Mg I (R)—Er Mn	84	Co I	26	Mn—
30	Cr—Er Pr	85	Pr Cr I (R) Co I Sm Zr Cb—Fe	27	Nd—Fe I
31	U—Ni I Ru Cb	86	Fe I (R) La II—Cr (R)	28	Sm—Cr I (R)
32	Mg I (R) Pd—Y	87	Fe I Er—Nd Bi	29	La Pr—Zr Ti I Os
33	Fe—Ta Mo I Mn Rh(R)	88	Er Bi—Fe I Cs I Ho	30	Fe I (R)—Eu Y
34	Fe I (R) Mn I (R)—	89	Pr Ba—Er Nd	31	Dy Ru
35	Zr I	90	V Zr U—Nd Er Nd	32	U Er—Fe
36	Os Fe Dy—Mn Gd Zr	91	Ho Zr I—Ba II (R) Fe	33	Sc I—Ca II (R)
38	Mg I (R)—	92	Nd Ru—Ba Er V	34	V Rh(R)—Gd Ir
39	Fe—Ru Mn	93	Fe—	35	Tb—Ba I Fe Rh Pr Co I (R)
40	Tb Os Fe I (R)—La V I Ag I	94	Cr I (R) Cb Co I (R) Pd(R)—Nd Gd Co I (R)	36	La—
41	Pr Fe I (R) Mn I Lu Cr Co I—	95	Ti—Fe I Gd	37	Er Nd—Ba I
42	Co I (R)—Tb	96	Er—Tb Ho Sm	38	Os Er Nd
43	Zr II Fe—Co Ho Mn	97	Au Fe Al	39	Tb
45	Co I (R)—	98	Fe I V—Dy Pt	40	Ho—Sr I Fe I Co I
47	V—	99	Tb—Fe I	41	Cr I (R) Nd Co I (R)
48	Nd—Nd Tb			42	Fe—Rh Ce
49	La Zr—Os Fe I			43	Mo—Cb
50	Ru—Gd Fe I Pr			44	Al I (R)—Tb Dy
51	Gd—IV Pr Nd Co			45	Co I—Gd Ru
52	Gd Fe I Pr			46	Ir—Tb
53	Ce—	3900	Nd Os—Ti II Pt	47	Pr Ti
54	Ho Cr—	01	Ru Tb—Os Mo I Nd	48	Fe Pt—Ti I Fe Ca I
55	V I Cr—Gd V I (R)	02	V I Gd Pr—Er Fe I Mo I (R)	49	La Pr—Fe
56	Fe I (R)—Rh(R) Co	03	Sm—Fe Er	50	Ru Y—
57	Os—Ru Cr	04	Y Ti	51	Nd Fe—Y V
58	Co Ni I—	05	Si I Ho Ho Nd	52	Gd Co I—Ce(R) Fe Ru Co I
59	Fe—U Fe I (R)	06	Co I Er Hg I Fe I—Nd	53	Gd—Pr
60	Cu—	07	Eu—Sc I Nd Fe	55	Y—
61	Co I (R)—Cu I	08	Pr Pr—Cr I (R)	56	Ce Ti I Fe—Fe
62	Ru	09	Ru Au—V(R) Ba I Co I	57	Ca I—Gd Dy Co I (R)
63	Nd—Zr I	11	Nd—Sc I	58	Nd Rh Ti I Zr Tb—Pd(R) Rh(R)
64	Mo I (R)—V I	12	Pr	59	Gd
65	Sr I Os—Pr Fe I U	13	Ti II—Rh	61	Co Mo—Al I (R)
66	Ti—	14	V Ti—Cb Ru Sc	62	Nd Pr—Ti I
67	Fe—Ru W	15	Li I (R) Ir Tb—Zr	63	Nd—Os Cr(R)
69	Mo I—			64	Pr Ti I—Rh Pr
70	Rh—				
71	La				

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
3965	Pr—Ru	4010	Ra—	4057	V Co I—Pb(R) Zn
66	Fe I Cb Pr—Pt Fe Zr	12	Nd Ce Cr—Tb	58	Co I Gd—Co I Cr
67	Fe—Y	13	Ru Gd Co I		Mn I Cb
68	Gd Dy Ca II (R)—	14	Sc Fe	59	Er Nd
69	Co Sr I Fe I Gd Er—	15	Er	60	La—
	Os Cr	16	W	61	Nd Ta—Tb
70	Sr I Ta—Sm W	17	Fe—	62	Mo Pb(R) Fe—Gd
71	Pr Fe Sm—Gd Eu	18	Mn I Os Y—		Cu I Pr
72	Pr—Co	19	Th—Pb(R)	63	Cu I Gd—Mn Sm
73	Co I Nd Zr—Ni I Er	20	Ir Sc I Tb Er—Nd		Fe I (R) V
	V Nd Ca I		Co I (R)	64	Ru—Zr Sm
74	Co I (R)	21	Nd—Nd Fe	65	Au I—
75	Rh Co—	22	Ru Gd—Cu I	66	Tb Co I (R)—Os Fe
76	Ir—Cr(R) Nd Tb	23	Nd Gd Rh Sm I	67	Fe La—Ru Ta Fe
77	Os—Fe		Co—Sc I Ru	68	Ru—Co I Ta
78	Ru—Dy Co I	24	Ti I Zr	69	Th Nd—Mo Ir
79	Sm Gd Ru Nd—Co I	25	Cr—La	70	Gd—Os
	Cr	26	Cr Mn—Ti Ta	71	Fe I
81	Cr—Zr Ag I Ti I Fe	27	Co I Cr Zr—	72	Zr
	Cd I Dy Tb	28	Gd Ti II—	73	Dy Gd Ce—Gd
82	Pr Nd Ti—Y	29	Zr	74	W—Os Fe
83	Sm—Dy Cr(R) Hg Fe	30	Sr I—Fe Ti Mn I (R)	75	Nd—Sm
84	Cr Rh—Ru		Gd	76	Cr Co I—Fe Ru
85	Mn—Li I U	31	La II Pr Nd Mn	77	La Y I—Rh Sr II (R)
86	Fe Nd Mo—Sm	32	Ru Sr I—Cb		Hg I Dy
87	Co I Gd—Er Ru	33	Ga(R) Tb Mn I (R)	78	Fe Ti I—Gd
88	La II		Cb—Gd Sb I Mn(R)	79	Mn I Mn I—Cb Pr
89	Pr Ti I Cr		Ir Pr	80	Ru(R)
90	Sm Nd Co I—V	34	Mn I (R)—	81	Pr Er Zr Y Mo—Pr
91	Zr Cr(R)—Co Cr Co I	35	Co V Mn I (R) Zr	82	Sc I Ti I—Rh Mn I
	Nd Co	37	Gd—Gd	83	Ce Pr—Mn I Y I
92	Ir—V Cr	38	Pd—	84	Au Mo—Fe
93	Ba I (R)—Ho Ce	39	Cr Ru Pr—Cb Gd Y I	85	Th Fe Eu Ru—Gd
94	Gd—Co I Nd Pr	40	Ir—Ce Ho Nd Au	86	Co I—Th La
95	Co I (R)—Rh Ba I	41	Mn I (R)—Os	87	Dy Pd—Er Gd Rh
	La Ru	42	U Sm La	88	Rh
96	Ta Rh Gd—Pt Sc I	44	K I (R) Hf—Zr Pr	90	U—Zr V I
	Pr	45	Gd Mn Co I (R)	91	Dy Os
97	Pr V Fe—Co I (R)		Ho—Zr Zr Fe I (R)	92	Pt Sm Co I (R)—V I
98	Fe Ho—Ti I V Zr		Tb		Ca I Gd
99	Er Ce—	46	Dy—Hg Hg I Er	93	Hf—
		47	K I (R)—Y I Sc I	94	Th—Th Ca I
4000	Pr Tb Ho—Dy	48	Er—Zr Mn I Cr	95	V I—Fe
01	Gd Cr—	49	Gd—Gd	96	Pr Mo
02	Tb	50	U La Zr—Dy	97	Rh Ru
03	Os	51	Nd Pr V Ru—Tb	98	Fe—Ca I Gd Gd
04	Os—Pr	52	Ru—Tb Co	99	La V I
05	Os Fe I—Tb Ru I	53	Gd—Ti II Ho		
06	Ru	54	Tb Ru Lu—Sc I Pr	4100	Er Pr Cb
07	Fe—Er	55	Zr Dy Ag I (R) Er—	01	Ru In I (R)
08	Pr W Ti I		Mn I	02	Mo V I Y I (R)—W
09	Ti Fe	56	Mo—Pr Cu(R)	03	Ho Tb

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
4104	La	4154	Rh—Fe Fe	4212	Gd Ag I (R)
05	Mo V I—	55	Mo Cb—Mo		Ru—Pd (R)
06	Ce (R)	56	Nd Zr—U Fe	13	Tb Zr
07	Sm Mo Fe—Rh Ru	57	Mo—Fe	14	Tb Ru—Cb Gd
08	Hg I Th—Ho	61	Zr Tb—Ru Sr II	15	Tb Dy W—Sr II (R)
09	Nd Mo Nd—Cr V I Fe	63	Ho—Cr Cb Ti U		Rb I (R)
10	Nd—Co I Y Mn	64	Pr—Pt Cb	16	Fe I—Hg
11	Dy Gd—V I (R) Pr	65	Sc—Ce	17	Gd Ru—La Y Cb
12	Os—Ru	66	Ba II Zr—	18	Dy—
13	V Pr	67	Ru Y I Mg I Dy	19	Fe—
14	Fe—	68	Pb (R) Cb—	20	Y Sm Ru
15	V I—Ir	69	Sm—Pd	21	Dy—
16	Rh V I—V I (R) Th	70	Gd—	22	Fe I—Ce
	Nd	71	W—U Gd Pr Ti	23	Pr—
18	Ce Pr—Fe Sm Pt	72	Ga (R) Fe Pr—Os	24	Ba Fe Y—
	Co I (R)	73	Os Ho—Gd	25	Gd Dy Sm Pr Fe—Gd
19	Cb Gd—Rh Ce	74	Y I—	26	Tb—Ge Ca I (R)
20	Mo Ho—	75	Ta Pr—Gd Nd W	27	Fe—Zr
21	Co I (R)—Bi I Rh (R)		Os Fe	29	Cb Ru—Ho Sm
	Bi I	76	Mn	30	Ru—La
23	Er La Cu—V I Cb	77	Nd—Y Cu Ra Ta	32	Ru Nd V—Mo V
	Nd Sm	78	Th—Nd	33	V Os—Fe I
24	Os Dy Lu Y	79	Cr V Pr—Zr	34	V—V Sm
26	Cr	81	Ta—Fe	35	Mn I Nd Mn I
27	Ho—Ti Fe	83	V—Dy Sm		Tb—Y II Fe I
28	V I Y I (R)—Rh (R) Os	84	Lu Gd—Fe Er	36	Pr—Ru Sm
29	Pr Cr Ta Cb—Eu Nd	85	Mo	37	Sm
30	Gd—Ba II (R) Pr	86	Ti I Tb—Ce Dy	38	La—Gd Fe
31	Mn—	87	Fe I Tb La—Zr Fe I	39	Zr—Ba I Mn I Nd Ce
32	V I (R) Fe I Gd	88	Sm Mo—	40	Pr Zr Ca I—
	Li I (R) Ba—Fe I	89	U—Pr V I Os Mn	41	Pr Ru Zr W—Zr U
33	Nd—Ce	90	Co I Cb		Au
34	Gd V I—Fe	91	Cr Fe I—Dy Pr	42	Ba
35	Mn Rh (R) Nd—Os	92	Cb La Pt Er—	43	Ru—
36	Ta—	94	Mo Er (R) Dy	44	W U Rh—Sm Ru
37	Fe Gd Cb W—Ce	95	Cb—Ni	45	Dy
39	Cb	96	Rh La	46	Mo Ru—Ru Sc II
40	Sc—	97	Ru Gd	47	Nd Fe—Pr
41	Mn Pr Dy—La II	98	Fe I—Cr Ce Ru	48	Ce Cu
42	Y I (R)	99	Zr Fe Y II—Ru (R)	50	La Fe—Fe I
43	Dy Pr Fe—Mo Fe I			51	Y—Gd Mo (R)
44	Ru Tb—Ce	4201	Ni Rb I (R)	52	Co Nd—
45	Ru	02	Fe I—	53	Gd—Gd
46	Dy—Ru	03	Sm—Fe	54	Cr I (R) Ho—
47	Fe I Ta	04	La—Y Gd	55	Ce
48	Pr—Mn	05	Eu V Cb—Nd Ta	56	Ti Dy Sm—
49	Zr—Mo Sm Ce (R)	06	Ru Sm—Dy Pr	57	Mn I
50	Al III—Zr	08	Th Zr	58	Zr Tb—Ru
51	Er Cb—La	09	Cr—V I	59	Ir Cu—
52	Sm Sc—Ho Cb Ho	10	Sm Fe I—	60	Gd Fe I—Os
	La	11	Rh (R) Nd—U Cb Dy	62	Gd Cb—Sm
53	Cb—Cr Fe I		Pr Os Zr	63	Ti Cr—La Pr

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

PRINCIPAL LINES BY WAVELENGTH

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
4264	Ho Ba I—	4310	Ir	4356	Ho Tb
65	Ra Sm—Mn I	11	Ag Cb Os—Ir	57	Y
66	Y	12	Mn Ti II	58	Nd Hg I—Dy Y II
67	C II—	13	Tb—	59	Ba Ni I Cr I (R) Zr
68	Ir—V Gd	14	Sc II Ru—Nd Ti I		Pr
69	Mo W La—	15	Fe—Y	60	Sm Gd
70	Cb	16	Gd Y—	61	Ru—Sr I
71	Fe I—V Fe I	17	Zr—	62	Sm—
72	Pr—	18	Ru—Ca I (R) Ti Tb	63	Cr—
73	Li I Th Rh—		Sm	64	Pt—Ce La W
74	Y—Ti I Cr I (R)	19	Sr I—Ru Sr I	65	Os
75	Nd Cu (R) Tb—La	20	Ce Sc II Ru	66	Y Ra Nd Zr—
76	Dy Tb Mo V	21	Gd—Ti	67	Tb—Ti
77	Mo I—Lu	22	La	68	Y I Pr Cb—Nd
78	Tb	23	Ba I Sm—Pr	69	Mo I—Gd Fe
79	Mo Ta—Sm	25	Sc II Ru Ti Ba—Gd	70	Gd Os Zr
80	Zr La Cr—Gd Sm		Fe I Nd Tb	71	Cr I (R)—Pr
81	Sm Lu Ma I Ti I—	26	Mo Os Ti I Cb	72	Tb Ru—
82	Th Zr Fe Pr—Nd Ti		Sr I—Mo I Ru	73	Rh Sm—Co Gd
83	Ca I (R) Ba I—	27	Pt Gd—Nd	74	Cr Dy—Sc II Dy
84	V Mn I Ru—Nd	28	Os		Rh (R) Mn Y
85	Co I	29	Sm Pr—	75	Nd Dy—Ce Fe I
86	Ti I Ta—La	30	V I—Gd Ho Y	77	Rb—Cb
87	Ru Ti I—U	31	Ru Gd Cb—Ni I	78	La Cu (R) Sm—Ta
88	Ni Pt—Mo I Rh (R)	32	Tb—V I Ba I	79	Ag V I (R) Y—Zr Rh
89	Ti I Ca I (R)—	33	Zr—La Pr	80	Mo I Sm—
	Cr I (R) Ce	34	Sm Ra—La	81	Mo Th
90	Ti II—Ti I	35	Pr	82	Ce—
91	Y Ti Ba—V	36	Tb Hf	83	La—Fe I
92	Mo I Sm Mo—Zn I	37	Fe I Ho Ru Y Mn—	84	Mg II V I (R) Sc II W
93	Mo I Ru—Mo I Os		Cr I (R) Eu Sr I Ce		Cr I (R)
94	Ti II Fe I—W (R)		Ti II	85	La Ru—Ru Nd
	Sc II Zr Ru	38	Tb—Pr Nd	86	Ru—Ce
95	Dy—Ti I Ni Ru	39	Hg I Cr I (R)—Co	87	Gd Y
96	Lu La V—Ce Zr Sm		Cr I (R)	89	Gd V I (R)
	Rh	40	Pb—Tb Ra II	90	Ru—Mg II Nd Sm
97	Gd—V Ru Pr	41	V I Zr Gd—U		Gd Fe
98	Zn I Gd—Ti I Eu Pr	42	Ru Gd—Tb	91	Ru Th—Ce Cr I Pt
	Ca I	44	Pr Gd Pr—Cr I (R) Y	92	Gd—
99	Ti Fe I Gd—Cb Ti I	45	Sm	93	U Ti
		46	Gd Ru—	94	Y Os Dy
4300	Ti II Y—Ti I	47	Gd Pr—Hg I Sm Zr	95	Ti II V I—Pr
01	Ti I Cb—Ir Zr	48	W—Y	96	Pr—
02	W Y—Ca I (R) Zr	49	Ru Ce	97	Os—Gd Ru
03	Nd	50	Mo I Ba Pr Sm—Ho	98	Y II Ta—
04	Nd—Ba	51	Cr I (R) Nd—Fe Cb	99	Ir—Pr Ti II
05	Sr II—Sc II Pr Ti I		Cr I (R) Pr		
06	V I Gd—Ce	52	Pr Mg I Y—Y Fe I	4400	Sc II—V I Nd
07	V I—Ru Ca I (R)		V I	01	Fe—Ni I Gd
	Ti II Fe I	53	Tb—	02	Ba Os
08	Bi I—Bi I Dy Tb	54	Ru La—Sc II	03	Pr Ir
09	Sm—Lu Y II V I	55	Ca I—U	04	Ti—Fe I

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
1405	Pr	4452	V La—Sm	4505	Ba Y
06	Pd V I (R) Gd Ba	53	Mn I Ti I—Dy Ti I	06	Gd—
07	V I (R)	54	Fe—Sm Ca I (R) Zr	07	Zr—
08	V I (R) Gd W Fe I— V I (R) Pr	55	Mn Mn Ti I Dy—La Mn Ca I (R)	09	Gd Ce(R) Cd—
09	Dy—Th	56	Ca I	10	Ru Pr—Th Ta
10	Ru Nb Ni	57	Mn Mo Ti I V I—Mn	11	Ru Pt Cd In I (R)— Th Sm Cr
11	Nd Gd—Mo Mn	58	Mn—Cr Sm	12	Mo I—Ti I
12	Sr	59	Ni I Fe I—V I	14	Y—Cr I Gd
13	Cd I—Ba Pr	60	Ce V I (R) Mn—H'	15	Sm—
14	Gd—Mn I	61	Mn—Fe I	16	Pd—Ru
15	Fe I Y—Sc II Cu Cd Ta	62	Mn V Ni I—Nd	17	Co Mo—Pr Ru
16	V I—	63	Ti	18	Ti I—Lu
17	Ti Hf Y—Ti II	64	Mn I Gd	19	Er—Gd Sm
18	Ce	65	Cr—Ti I	20	Pt Ru
19	Gd Cb—Er Pr Mn	66	Gd Fe Co I	22	La—Eu Er Ti I Gd
20	Os—Sm Ho Cb Ru	67	Gd Ba Sm—	23	Pt Ce Ba Cb—Sm
21	Sm Pr Gd Co I Ru—V I	68	Mo—Ti II Dy Pr	24	V Mo I—Sn Os Ba II
22	Gd—Fe Y II Ti	69	Nd Fe—Co I V	25	Fe La—
23	Tb—Mo La	70	Mn I Ni I—	26	La II Mo Cr—Er Ca I
24	Cr Sm—	71	Ce Ti I Cb—Co I	27	Y Ti I Ce—Dy Y
25	Ca I (R)—Ra	72	U—Mn I	28	Ce—Fe I Rh
26	V I Ti Ir—Mo I Er	73	Sm—Er Pd Y Ru	29	Os
27	Ti I Fe—La	74	V Gd—Mo V Ti	30	Cr Ta Cu I Ru Co I
28	Mg II Gd Ru—V I	75	Y	31	Er Fe I Sr—Ho Ru
29	Pr Ce—V I La	76	Fe Ag I Gd—Y Tb	33	Ra II Ti I (R)—Ti II
30	Fe I Gd	77	Pr Y—Ho	34	Co I Tb Pr—Ti I (R)
31	Ba	78	Ir—Sm Gd	35	Ti I (R) Cr Zr I Pr Ti I (R)
32	Rh—	79	Ce—Ti I	36	Ti I (R)—Mo
33	Sm	80	Cu I Ru—Sr	37	Tb—Gd Sm
34	Mg II Ti Sm—Mo Ca I (R)	81	Ti I Er—	39	Cu Ce Os
35	Eu Ca I (R)	82	Fe Fe I—Ti	40	Cr
36	Tb V I Gd Ra II Os Mn—W	83	Gd—Co I	41	Pd Nd—
37	Au Pt Y—V I	84	W Fe—Pt Os Mo	42	Sm Cr Mn—Nd
38	Sr I Gd—	85	Ce	43	W U Co I Sm
39	Ru	87	Mo Y Y—	44	Rh Y—Cr Ti I Er
40	Ti Zr—	88	Au Ti Ru—V Ba I	45	V—Ir Cr I (R)
41	Tb—V I	89	Ti I Pd—Fe I Er	46	W—Cb Ni
42	Mo Fe I—Pt Zr	90	Mn I—	47	Ru—Fe Ru Pt Gd
43	Mo I Fe—Y Ti II	91	Mo—Y	48	Ir—Mn Os Rh Ti I
44	V I Sm—Ru Ce	92	Rh—	49	Fe II—La Ti II V Co
45	Pt	93	Tb—Ba I	50	Os—Gd
46	Nd Gd—Y	94	Fe I	51	Os—Rh W Ta
47	Cb Os—Fe I	96	V Ti I Pr—Cr I (R) Zr	52	Ru Er Pt Ti I—Sm
48	Er	97	Gd—	53	Zr I V—
49	Ti I Ce Ru—Dy Mo Pr	98	Ru Gd—Pt Mn I	54	Zr Ba II (R) Sm—Pt Ru(R)
50	Ce Ti I	99	Sm—Zr	55	Cr Zr Cs I (R) Y Ti I—
51	Nd Mn I Nd	4500	Er	56	Ag Fe—
		01	Ti II—Nd V	57	Rh—
		02	Mn I—		
		03	Cb Dy Er—Rh Mn		

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
4558	Gd Mo I La—Cr Rh	4612	Dy—	4665	Na I Er—
59	La Y—	13	Fe I W Cr I La II—	66	Cr
60	Pt Ce Sm—V Rh	14	Cd I Gd—	67	Cb Fe—Ti I
62	Ce—	15	Sm—Cd I Sm Ag Er	68	Fe I—Ag I La
63	Pr Nd Er—Tb Ti II	16	Cb Cr I (R) Ir—Os	69	Na I Ta Fe Cr Sm
65	Rh—Cr I Co Ta	17	Ti I—		Tb—Sm Ru
66	Sm—Gd	19	Fe—Th Ta Cr V I	70	Sc—V I Sm Gd
67	La		La Rh Ba I	71	Mn I La
68	Ir—	20	Hf	72	Pr Cb—
69	Rh—Cr	21	Mo—	73	Fe—Ba I
70	La Co—W	22	Cr—	74	Sm Ru Cu Y I
71	Mg I Rh—Cr V Ti II	23	Ti I—	75	Rh Ti Cb—Er
72	Ce—Be I	24	Th Dy—	76	Tb Sm
73	Cb—Y Gd Ba(R)	25	Fe I—	77	Rh Pd—Ag
74	Ta—La	26	Cr I (R) Zr	78	Cd I (R) Sr I—Fe
75	Zr La		Mo I—Mn	79	Er—
76	Mo I—	27	Ur Eu Mo—	80	Gd Zn I (R)—W
77	V I Pt—Sm Dy	28	Ce Ba I—Pr	81	Ru Tb Ta Ti I
78	Ca I Tb V Nd	29	Ho Ti I Co I—Zn I	82	Dy Ra II Y Co I—
79	Os Nd Cb—Ba(R)	30	Cb Fe—Er	83	Gd Zr—
80	La Cr I Co V I	31	Th Os	84	Ru Pt—Ce
81	Ca I—Co I Cb	32	Tb—Fe I	85	Ca I—Ge
82	Gd	33	Zr	86	Ni I Gd—V
83	Fe II	34	Nd—	87	Sm—Zr I
84	Ru—Sm	35	V I—Ru	88	Zr—Tb Er
85	Ca I Ca I	36	Li I—Tb Gd	89	U Cr—
86	V I—Gd	37	Tb—Fe I	90	Ru—
87	Cu—Tb	38	Fe—Gd	91	La Ti I Fe—Ba(R)
88	W	39	Rh Ti I—Cr Ti I Ti I		Ta
89	Dy—Ba I	40	Er Pt	92	Os La—
91	Ru V Cr I—Tb Ba I	41	Tb Ra—Tb	93	Tb Co I Ta—W
92	Ru Ni I Fe I	42	Sm—Mn	94	Gd—
93	Ca I (R)—Sm Ce	43	Rh Fe—Y I	95	Pr
94	Eu V I (R)—Co	45	Ru Ti I Tb—Nd	96	Y
95	Os Mo I Sm Th Cr—	46	Cr I (R) V I—U Sm	97	Er Gd—Cu
96	Y Ru Co Gd	47	Tb Fe—Ru	98	Co I Cr—Dy Ti I
97	Os—Gd	48	Ni I Cb	99	Ra—
98	Hf Gd	49	Ho		
99	Ru—Ba(R) W	50	Ti I—	4700	W Ba I—
4600	Cr V Ni I—Cr I (R)	51	Cu Cr I—	01	Mn I—Ni
01	id—	52	Cr I (R)—	02	Er Gd Tb—
02	Li I (R)—Zr Th Gd	53	Gd	03	Mg I Gd—Ni
	Fe I	54	Ce Ru—Fe I Fe I	04	Rh Sm—Cu Fe
03	Li I (R)—Cs	55	La—	06	Cb V—Nd V
04	Tb Sm—Y Ni I	56	Ir Ti I—Er	07	Mo Fe I—Tb
05	Mn—La	57	Pt	08	Cr Mo Cb—
06	V I Ce—Er Cb	58	Lu Y—Y	09	Ru—Mn I Nd Gd
07	Sr I (R)—Fe I	59	W	10	Zr I Ti I Fe—V
08	Rh—	61	Ho—Eu Mo I	11	Zr
09	Mo I W	62	Cd I—La Mo I Tb	13	Cb—
11	Er Fe—Er	63	Co I—La Os Cb Cr	14	Ce Ni I—
		64	Cr	15	Nd Ni I

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
4716	Tb Pd La—	4771	Co I—	4830	Eu—Mo
17	Zr V Mo	72	Zr I—U Fe I	31	Er Ni I—V I
18	Cr—Eu	73	Mo—Ce	32	Sr I V I Dy—Th
19	Zr—La	74	Th—	33	Ru Cb—Dy
20	Rh	75	Dy	34	Er
22	Zn I (R) Bi Sr I—Bi I	76	Co I V—	35	Gd—
	Bi Er	77	Sm	37	Tb
23	Th	78	Ir—	38	Ru
24	Nd La II Cr—Er	79	Sc I Er—	39	Lu Y
25	Ce—	80	Co I—Ta	40	Co I Dy—Ti
26	Ba I—	81	Y Gd—Gd	41	Sm Dy
27	Dy Cr Mn I—	83	Sm Pr Mn I Gd—	42	Er Rh—Tb
28	La Gd—Y Ir Dy	84	Sr I—Gd Zr	43	W—Os
29	Er Se I—	85	Lu—Sm	44	Rh Sm—Ru Tb
30	Mg I—Cr	86	V I Ni I Y II Tb Gd	45	Y Dy
31	Ti (R) Ru Mo—U Er		Fe Dy	48	Gd Ag Cb Sm—Er
	Dy	88	Pd—Zr I	49	Eu
32	Zr Y—Gd	89	Cr—Fe Tb	50	Th—
33	Ru Fe I Bi Cb	91	Sm	51	Zr I—V I Rh Er
34	Sc I Tb—	92	Cr Eu Au Co I	52	Y
35	Gd	94	Os—	53	Er—Pt
36	Pr Fe I Er	95	Er Ir	54	Er—Y II
37	Ce Cr—Sc I	96	Mo V I	55	Sr I Ni I—
38	Os—	98	Rh	56	Ti I Ra Dy—Gd
39	Mn I Zr I—Tb	99	Y—Cd I (R)	57	Er—
40	Ta La Th—			58	Th Er—
41	Sc I Pd Y—Fe Sr I	4800	Hf	59	Nd—Fe I V
42	Ho—Ti I	01	Gd Cr—Tb	60	La
43	La—Cd Sc I Os	02	Br—	61	Er Gd Cr
45	Rh Er—Sm Gd Dy Fe	04	La Y—Y Ru	62	Mn—
47	Tb	05	Ti I—Zr I	63	Th—
48	Na—La	06	Tb	64	V I (R)
49	Co I	07	Gd—V I	65	Gd—Nd Os Rh
50	Mo—	09	La Zr—	66	Ni I—
51	Er	10	Rh—Zn I (R) Cb	67	Eu Co I
52	Na I Cr Os Th—Tb Y	11	Mo Nd—Au I Sr I (R)	68	Mo Dy Ti I—Sr I
53	Sc I—	12	Ta	69	Ru Sr—
54	Mn I Co I—	13	Co I—Tb	70	Ti I—Cr
55	Rh	15	Ru Zr I Sm Os	71	Fe I—
56	Cr Ru Ir—Ni I U	16	Cb—	72	Er Fe I Sr I Er—Th
57	V I W Ru	17	Pd—Pd	73	Ni I—
58	Ti I—Mo Cu Gd	18	Th	74	Ag—
59	Ti I—Er	19	Mo U—Y	75	Pd V I (R)—Tb
60	Mo Sm—Gd	20	Er Ti I—	76	Sr I Tb Sr I—
61	Y I Er Th—Mn I	21	Gd	77	Ba I
62	Tb Mn I—Er Zr	22	Y—	78	Ca I Fe I Er—
63	Os—	23	Y II—Mn I	79	Pt Er
64	Cr—	24	La Zr I—	80	V
65	Mn I	25	Dy Nd—Ra I	81	Tb—V I (R) Gd
66	Mn I—V I La	27	V I—	82	Ce—Co I
67	Gd—	28	Zr—Dy	83	Zr Y II Er Sm
69	Ru—	29	Ni I Cr—Dy	85	Ti I Tb—

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5Å; no dash indicates greater than 0.5Å.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
4886	W	4957	Fe I Dy—Fe I	5016	Ti I—Cu
87	Cu—	58	Ru—Gd	17	Th—Ni I
89	Dy—	59	Zr—	18	Hf Ni I Fe II—
90	Dy—Cb Fe I	60	Eu—	20	Ti I—
91	Fe I	62	Sr I Tb Se—Eu	22	Dy Tb Fe—Ce Ti I
92	Sr I—	63	Rh		Eu
93	Y—Dy Ce Sm	64	Th Tb—	24	Ti I
94	Gd—Th	65	Mn—	25	Ti I
95	Ru	66	Fe I—Co I	26	Cb
97	Tb—	67	Ho—Cb Sr I	27	U—Dy
98	Er—	69	Gd—	28	Th Er
99	Os Dy U—Co I Ti I	70	Th La Ir—Tb	29	Eu
	La Ba II	71	Ce Sr I Ra Pd Li I	31	Sc—Os
			Co I	32	Dy
4900	Er Y II—V Eu	73	Cb—	33	Pt Eu
02	Ba I	74	Y—Dy	34	Cu—
03	Ru Ra Cr Fe I—	75	Ti—	35	Ni I—Ti I
04	Co V Ni—Lu	76	Ru Er—	36	Ti I—
06	Y—	77	Rh	38	Ti I—
07	Eu—	79	Na I Mo Rh—	30	Cb—Ti I
08	Tb—	80	Tb Ni Ru—Tb	40	Hf
09	Zr	81	Ti I Ir	41	Fe I Ra—Ca I Fe I
10	Sm—	82	Ra Y II—Fe W	42	Er Tb Ni I—
11	Eu—	83	Fe Na I—Fe	44	Ce Pt Sm—
12	Th Zn II Os	84	Ni I—	46	Ir—Zr
13	Ti I	85	Fe—Fe I Mn	48	Ni I
15	Tb	86	La Tb	49	Th Fe
16	Hg I Dy—	87	Th—	50	Gd
19	Fe I Sm—Th Pd	88	Cb	51	Fe I
20	Fe I Nd La	91	Ti I—	53	Dy W—
21	Ru—Th La Y	92	Er—	54	Tb—W
22	Dy Cr—	93	Tb	55	Th—
23	Dy—	94	Lu Fe I—Zr	57	Ru—
24	Zn II Tb—Fe Cb	95	Tb	58	Cb—Th
25	Er—V	97	Tb	59	Pt—Mo
28	Co I—Tb	99	Gd La—Ti I Ir	63	Pd—
30	Gd			64	Rh—Au I Ti I Zr
31	Tb Er	5000	Ni I Er—	65	Fe Zr—Tb
34	Ba II (R)—	01	Ti I Lu—Fe	67	Th
35	Ni I	02	Ir	68	In I Fe I
36	Cr Ta Ti I—	03	Dy	69	W Sm—
37	Ni—	04	Ir—Mn	70	Y Se—
38	Ir Ru—Gd Fe I	05	Pb—Fe	71	Sm—W
39	Ir—Fe I	06	Fe I W—Y	72	Ru
40	Tb—	07	Ti I Er—	75	Co—
42	Cr—	08	Er	76	Cu Ru—
44	Er—	09	Ir—	77	Er
47	Ba—Tb	11	Ru—	78	Zr—Tb Cb
49	La	12	Fe I—	79	Fe I—Ce Fe I
50	Mo	13	Eu Cr—	80	Mo—Ni
51	Er	14	Ti I—Ru Fe	81	Ra Ni—Sr I
54	Th Cr	15	Ir Gd W—Th	83	Fe I—Se I

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
5084	Ni K I (R)—	5153	Cu I—Na I	5211	Zr Rh—La
85	Rh Sc I Cd I (R)	54	Cd I	12	Rh Co I Er
87	Sc I Y II—	55	Ru Dy Zr—Rh Ni I	13	Sr—
89	Tb—		Gd	14	Cr—
90	Dy—Rh Fe	56	Sr I—	15	Eu Er Fe I—
92	Gd—	57	Rh—	16	Fe I—
93	Ru	58	Zr—Rh	17	Fe I—
95	Th Cb—	59	Ba	18	Cu I Er—
97	Fe Ra—K I (R)	60	Eu Cb—	19	Pr Gd—Ti I
98	Fe I	62	Fe—	20	Cu I Pr Ni I—
99	Sc Ni I K I (R)—Ni I	63	Pd	22	Sr—Rh
		64	Cb—Er	23	Eu—Ru
5100	Cb Sm—	65	Dy—	24	Ti I W Cr Ti I
03	Sm Gd As—	66	Cr Fe I—Eu Dy	25	Sr—
05	Cu	67	Mg I (R) Fe I—	26	Ti II Fe I
06	La—	68	Ni I Fe I	27	Fe—Pt
07	Ru Fe I—Fe I Dy	69	Dy	28	Tb—
08	Gd	71	Ru La—Fe I	29	Sr Er—
10	Pr Fe I—Pd Pr	72	Mg I (R) Er Mo I	30	Co I Au—Rh
11	Cu	73	Mo—Ti I (R) Pr	32	Cb Fe I
12	K I (R)	74	Mo I—	33	Th—
13	Ti I—	75	Ba Rh	34	V La—Pd
14	Eu Pd—La	76	Co Gd—Ni Ir	35	Co—
15	Ni I—	77	La—	37	Rh Cb—
17	Pd Ce—Mn	80	Cb—	38	Mo I—Sr Ti Ir
19	Y II—	81	Hf Zn	39	Sc
20	Dy Cb Ti—	82	Zn I—	40	Y Mo I
22	Co I La	83	La—Mg I (R)	42	Ru Fe—
23	Y—In Fe I Nd	84	Rh—Cr	46	Er—
25	Ni I—	86	Tb—Cb	47	Cr I (R) Th Co I
26	Co I	87	Ce—	48	Tb
27	Fe I Er—	88	Ti II Ca I Er	49	Nd
28	V	89	Cb—	50	Fe I
29	Eu Ti II Ni I—Pr	91	Fe I—Zr Ce	51	Gd—Ru Cb Sm
30	Nd	92	Fe I—Nd W Ti I (R)	52	Ti I—
33	Co—Eu Fe Er	93	V Cb Rh—V	53	La—
34	La—Cb	94	V Fe I	54	In I—
35	Lu Pr Y—	95	Ru Pr Fe—Cb	55	Cr Mn Nd—Ti Er
36	Ta—Ru	96	Y Cr—Mn	56	Pd—Sr
37	Ni I Fe—	97	Mn—Dy Gd	57	Er Ru—Co
38	V—	98	Fe I	58	Sc—
39	Fe I Fe I—Dy	99	Eu	59	Mo—Pr
41	Ca			60	Ca I—Dy Mn
42	Fe I Ni I Ru Fe I	5200	Y II—Sm	61	Ca
45	Mo I La Ti I—	01	Pb—	62	Tb Ca—
46	Ni I—Co I	02	Fe I—Os	63	Fe I—Pr
47	Ru Ti I—	04	Cr I (R)	64	Cr I (R) Ca I—
48	Th—V	05	Y II	65	Os—Ca Cr I (R) Ti I
49	Na I Er—Os	06	Cr I (R)—Er Pr	66	Co Eu Co I—Fe I
50	Fe I	08	Cr I (R)—Fe I Pd	67	Ba I—
51	Ru—Th Fe I	09	Ag I (R)—	68	Co I—
52	Ti I—	10	Ti I (R)—Sc	69	Rh—Fe I

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
5270	Ca I Fe I—	5337	Cd II—	5402	Ta Lu Eu Y
71	La Sm—Cb Eu	39	K I (R) Fe I	03	Sm
72	Dy—Er	40	La Ir	04	Fe—Rh
73	Fe I Nd—Ir	41	Fe I Mn I Sm Co—	05	Sm—Fe I
74	Ce—	42	Co Se I	06	Ra
75	Cr I—	43	K I (R) Co—Er	07	Mn I—Co Zr
76	Er Cr I Co Cb—	44	Cb Er—	09	Ce—P Cr I
77	Th—	45	Pd—Cr I	10	Fe
79	Er—Mo	48	Er Cr I—W	11	Ni—
80	Cr U—Co I	49	Se I Ca—Mn	13	Gd—Mn
81	Tb—Fe I	50	Gd Ti I (R)—Cb	14	Er
82	Ti I—Sm	51	Ti—	15	Fe V—
83	Ti I—Fe I Gd	52	Co I—	16	Os—Os
84	Ru—	53	Gd V Co—Ce	18	Ru
85	Zr Cb—Se	54	Rh—Tb	19	Dy—Er
89	Y II	55	Eu—	20	Mn I—
90	La	56	Sc Rh—Nd	21	Lu
92	Rh—Cu Pr	57	Eu La	22	Er
93	Nd—	59	Co—K I (R)	23	Dy—
94	Pd—	60	Mo I	24	Rh Fe V Tb Y—
95	Pd Ti I	61	Nd—Eu Ru		Ni I Rh
96	Cr I Zr	62	Zr Pd Co Rb I	25	Rb—Th
97	Ti I Cr I—Cd I Cr I	64	Mo I Ir—Fe	26	Ti—Dy Eu
98	Hf Pr Cr I Ti—Os	67	Fe—	27	Ru
		68	Sm—Er Pt	29	Ti—Fe I
5300	Cr I	69	Co I Ti Tb Fe	31	Nd Rb I
01	Pt Co I—Dy Gd La	70	Gd	32	Mn I
02	Er Fe I—Ta La Ba	71	Ni Fe I—	34	Fe I
03	La	73	Hf	35	W Pd—Th Ni I
04	Ru	75	Sc—Tb	37	Cb—Mo Lu
07	Gd—	76	Os Eu	38	Y—
08	Zn I	77	La Mn—Mn Ru Tb	41	Rh—
09	Dy Ru—	79	Rh—	43	Os—
10	Zn I—Zn I	80	Y Dy La	44	Co—
11	Zr—Hf Dy	81	Pr—La	45	Rh—
12	Pd Co	83	Fe—	46	Sc—Fe I
14	Rh	85	Zr—Ru	49	Ir
16	Gd	86	Cr	50	Sr I
18	Cb	87	Cr	51	Dy—Eu
19	Tb—Nd	88	Mn	52	Eu
22	Pr	89	Ta Gd—Dy	53	Sm—
23	K I (R)—Ag	90	Ti Rh—Pt Ir	54	Er—Ir Co Ru
24	Fe I—Dy	91	Cu	55	La Dy—Fe I
25	Th Co—	92	Sc—Eu	56	Ru—Er
28	Fe I Er Cr I—Fe	93	Fe I Ce—Gd	57	Mn I—
29	Cr I—Rh Cr I Ag Sr I	94	Mn I Pd	59	Tb
30	Ce	95	Pd—Dy Er	60	Hg I (R)
31	Co I—	97	Ti Fe I—	61	Ta—
33	Gd—	99	Mn	62	Er Ni—Th
34	Er—Ru Cb			63	Fe Hf—
35	Ru	5400	Ra	64	La—
36	Ti	01	Ru Ru—V	65	Mo Ag I—

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLES AND CHARTS

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
5468	Fe Y—Sm	5521	Y Sr I	5577	Eu Y(R)—
67	Sm—	22	Ce—Pr	78	Ru—Ni I
68	Y—	23	Co—Os Cb Ag	80	Eu—Os
69	Gd Pr	24	Tb Pr—Co	81	U Y(R) Ca
70	Tb—Mn I Rh	25	Tb Pt	83	Gd
71	Ti I—Ag I	26	Sc	84	Os—V I
72	Co Eu—	27	Y(R) U	86	Fe I Cb
73	Mo Y—Ba Fe	28	Dy Ti I Zr Mg I—	87	Ni I
75	U Pt	29	Pd—	88	Sm La(R)—
76	Fe Lu Ni I	30	Co I	90	Ca I—Co I Cb
77	Co I Er—Ti I W	31	Pr—	91	Gd
78	Sm—Pt	33	Mo I—Nd	92	Ni I V I—
79	Ru—	34	Sr I	93	Ba Er—Ni I
80	U Ru—Y Sr I	35	Rh Gd Pr—Ba I (R)	94	Gd—Ca I Pd
81	U Mn I Ti I—Ti I Sc		La Cu	97	U—
82	La—	37	Sm—Mn I	98	Er Ca Ce—Cd I
83	Co I—Co I	39	Th	99	Bi Rh—Sb
84	Rh Ru—Sc	40	Sr I		
85	Sm—Nd Er	41	La(R)—	5600	Ni I—Dy Sm
86	Sr I—	42	Pd	01	Er Ca I Ce—Pd
87	Fe V	43	Sr I—	02	Sb—Nd Ca Fe I
88	Ti I—Eu	44	Rh Y Gd Pr	04	Th—Cd I V I
89	Co	45	Ag	05	Pr Dy
90	Ti Sb—Sm	46	Y—	06	Y—
91	Y—	47	Pd V Dy Eu—	08	Pd Rh—Pb
92	W—U	48	Gd Nd—Sm	10	Pr—U Mo
93	Y—Sm Mo	50	Sm(R)—Hf	11	Mo
94	Nd—	51	Cb—Mn	13	Dy—
95	Eu—Y	52	Hf Bi—	14	Nd—Ce Ni I
96	Ru Pd	53	Ho Sr—	15	Fe I
97	Y—Fe I	54	Tb—Fe Cu Tb	17	Gd
98	Sm	55	Ra	19	Pd—
		56	Sb Mo Tb Y(R)—	20	Ir Zr—Nd
5500	Gd—	57	Al I—Al I	21	U Sm
01	La(R) Fe I—	58	Co	22	Eu—
02	Zr—	59	Gd Ru	23	Pr—
03	Y W—Ti I	60	Gd	24	Fe I V I
04	Sr I—Cb Rh	61	Nd—	25	Ni—Ir
05	Ta Er Mn I	62	Pr—	26	Sm V I—Er
06	Mo I Fe I	63	Fe	27	Dy—V I
07	V	64	U Th—	28	Cr
09	Pr Os—Tb Y Ni I	65	Ti I—Fe Tb	29	Cb—Gd
10	Eu Ru	66	Ho	30	Y(R)
11	U	67	Mn	31	La—W Sb
12	Ce Sm—Ti I Cb Ca I	68	Sb La—	32	Gd Mo I—Eu
13	Pr	69	Ru—Fe I Nd	34	U—
14	Pt Sc Ti I—Tb Ti I W	70	Eu Mo I—U	35	Cs—
15	Dy—	71	Pr	36	Co Ru—
16	Sm Tb—Mn I	72	Fe I	37	Ni Cd—Co
18	Ta	73	Sm—Mn	38	Fe—Pr
19	Ba I (R)—Sm	75	Er	39	Dy Th Sb
20	Sc	76	Fe I Cb—	40	Ho Sc II

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
5041	Dy	5700	Sc I Cu I Rh—	5756	Pr—
42	Cb—Pd	01	Gd—Fe	57	Er
43	Gd—	02	Nd Ru Cr—Ti I Dy	58	U—
44	Sm Ti I—Y(R) Gd	03	VI (R)	59	Sm Pd
45	Eu Ta	05	Mo	60	Cb—Th Ni I
46	Dy VI—	06	Sm Cb—Y(R) Ho	61	La(R)
47	Co—	07	VI (R) Th Sb—Pr Dy	62	Ti—Er
48	Rb I La W Y(R)—	08	Nd Ti I—Sc I	63	Fe—Pt
50	Mo I—	09	Ir Fe I Sr Gd—Ni I	64	Cb
51	Dy		In I	65	Os Eu—Y
54	Rb I—	10	Er Sm	66	Ti—Dy
55	Ce Pd—	11	Mg I—Sc I Ni I Ti I	67	Sr—
56	Sm—Au	12	La—Sc I Cr Ru	68	Ir Ce
57	VI—Sc II	13	Ba	69	La(R) La(R)—Hg I
58	Fe I	15	Ni I Ti I Ta—		Er La(R)
59	Co—Rh Sm	16	Cb Ti I—	70	Co—
60	Ra W Sb	17	Sc I—Fe	72	Zn I—
62	Ti I—Fe Ti I Y(R)	18	Nd Mn Dy—	73	Ce—Sm
63	Cs I (R)	19	Ce Hf—	74	Ti—Sb
64	Zr Cb Ta	20	Mn Ti I—	75	Fe Lu—Zn I
65	Ru Er—Cb	21	Sm—Os Gd	76	Gd—V Ta
66	Ag—	22	Mo I	77	Zn I—Ba I (R)
67	Tb	23	U	78	Ir Sm—
68	VI Pr—Nd	24	Sc I—Rb I Gd Ru	79	Sm Pr—
69	Sc II U—Ce	25	Ir—V Ru Ce	80	Mn—U Ta Os
70	Pd—V	26	Nd	81	Cr—Y Cr Sm
71	Cb Dy—La Sc I	27	VI (R)—VI	82	Cu I—Ru K I (R)
73	Eu	28	In I—Dy Y	83	Cr—Eu Cr
74	W—Ho	29	Cb Nd—	84	Cd—
75	Y Ti I—Na I Nd	30	Sb—	85	Cr Tb Pr—Cr
	Hg I	31	V—Sn Fe	86	Ti V Pr—
77	Dy Ce	32	Cu—Sm	87	Sm—Cb Cr
79	Ru	33	Gd	88	Ce Sm—U
80	Ba—Zr I	34	V—	89	La(R)—
81	Pr	35	W—	90	Hg I (R)
82	Ho Ni Cr—Na I	36	Ir—Lu Pd	91	Pr Er La(R) Gd—
84	Sc II—	37	VI—		Mo I
85	Dy Tb	38	Sm Mn—	92	Rh
86	Rh—Sm Sc I	39	Er Ti I—Pd Ti	94	Cb—
87	Pr Ir—Sm	40	Dy—La(R) Nd	95	Tb Rh
88	Na I Pr Nd—	41	Fe	97	H—
89	Mo I Ti I—	42	Nd—Bi	98	La(R) Zr I
90	Pd—Pr	43	Sm V I—Ce Y	99	U
91	Sb U Ho—	44	La(R)—Tb		
92	Pb—	45	Ru	5800	Eu Ba I—Sm Os Lu
93	Sr—	46	Gd—	01	K I (R)
94	Cr Ni	47	Ru—Tb	02	Sm
95	Pd—	48	Sn—	03	Tb Rh—Hg I
96	Gd—Sm Cu	49	Nd W Th Gd—	04	Nd Th Ra Ti Ce—W
97	W	51	Ho Mo I Cb—Cd	05	Ni I—Dy Ba(R)
98	Cr—V I (R)	53	Fe—Sn		La(R)
99	Ce—	54	Gd—Ni I	06	Rh Ir

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLES AND CHARTS

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
5807	V—	5868	Dy—Sm Pr Nd	5930	Fe—Pr La(R)
08	La(R)—	69	Mo—	32	Sm Ru Ru—
09	Gd—	70	Gd—Th Tb	33	Ho
11	Ta—Nd	71	Sm—Ce	34	Cb Ce—Fe
12	K I (R)—Ce	72	Er Ir—	35	Co I—
13	Ra II	73	Eu Ir—	36	La—
14	Sm Ru	74	Sm—Cb	39	Sm—Ta Pr
15	Pr Cb Th—	77	Gd Ta—Cb	40	Ce
16	Fe—Sr Mn	78	Pr—	41	Rh Ti I
18	Pr Eu Ba I	79	Pr—Zr Y'	44	Th—
19	Cb—	80	La(R)	45	Y Ir Dy
20	Pr	81	Er—	46	Co
21	Rh Y La(R)	82	Ta Ir—Ho	47	W
22	Pr	83	Fe	48	Ho—Si I
23	Pr La(R)	84	Cr—	50	Y—
25	La—Nd	86	Er	51	Pr—
26	Ba I (R)—Er	87	Ir—	52	Fe
28	Ru—Ir	88	Mo I—	53	Ti I—
29	La(R)	89	Na I (R)	55	Ho
30	Co—V Eu	90	Co—	56	Pr Fe I
31	Rh Ni	92	Pr—Ho Ni I	57	Aw—
32	K I (R) Y—	93	Mo I Cb—	58	Er
33	Ru—	94	Ir Zn II—La(R)	61	Tb—
34	Cb	95	Pb Mo I Na I (R)	64	Ba
35	Pr—	97	Sm—	65	Sm Ti I W
36	Sm—	98	Tb Sm	66	Eu—
37	Au I—U	99	Ti I	67	Eu Tb—
38	Ce—Cb			68	Sc—Sm
39	Ho—	5900	Cb	69	Sc—
40	Pt—	01	Ta	70	Sr I Sn—
42	Nd—Cb Tb	02	Er—Sm Hf Y'	71	U Ba I
44	Sb Os(R) Pt Pr	03	Sm Os	72	Ho Eu
45	La(R) U—	04	Gd—Gd	73	Ru—Th Ho
46	Ir V—	06	Er—Nd	74	Dy
47	Pr—	07	Rh—Ba I	75	Th Fe—Ce
48	La (R)—Mo Mn	09	Er—Nd	76	U—
49	Mo	10	Co—	78	Ti I
50	Er—Pr	12	Sb—Sm	81	Co
51	Tb—Mo Gd	13	Gd	82	Ho
53	Ba II (R) U	14	Fe Th—	83	Nb—Rh Lu Ir
55	Er—La(R)	15	Dy U—Co Eu	84	Lu Co I—Fe Dy
56	Gd—Pr	16	Fe—	86	U—
57	Ca—Ni I Os	17	La	88	Mo Sc—
58	Mo I—Nd	18	Rh—Ti Ta	89	Th—
59	Hg I—Th Pr	19	Ru Sm—	91	Rh—Co
60	Ho Sm—Lu Pt	20	Pr	92	Eu
61	Tb—	21	Sm Ru—Ho	93	Ru
62	Ce Fe—Au	22	Ti I—	94	Nd
63	La	23	Sm—	95	Os
64	W	25	Sn—Th	96	Nd—Ni I
66	Ti I—Cb	26	Mo I—	97	Ba I (R) Lu Th U—
67	Ca Sm	28	Ce—Mo I		Cb

Intensity (Ba 10 to 8; Ca 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
5999	Ti I	6059	Pb	6122	Ca I (R)—Co
6000	Co	62	Ho	23	Hg—Ce
02	Pb Ho—	63	Ba I (R)—	24	Eu
03	Fe—	65	Fe—	26	La (R) Ti I—
04	Eu—Lu Gd	66	Nd—	27	Zr I—Fe
05	Sb—	67	Ir	28	Rh W—Cd I
06	Co Pr—Er	68	La (R)	29	Ba—La (R) Sb
07	Ni I La—Nd Co Y	69	Sn Ce—	30	Pd
08	Fe Dy	70	Sm—Co Rb I	33	Ho Dy
09	Y—	71	Nd	34	La (R)—Zr I Bi
10	Cs I—Dy	72	Hg I	35	V I—Cr
11	Pb	73	Th—Sn Nd	36	Fe
12	Ni—Eu W	75	Eu	37	Fe
13	Ce—Mn I	76	Er—	38	Y I—
14	Gd—Er	77	U—	41	Ba II (R) Ir
15	Th—Er Os	78	Mn Fe—	43	Zr I—
16	Pr Mn I	79	U—Mo Sb	44	Os
17	Sm—Pr	80	Gd—	46	Sc—
18	Eu—	81	V I—Ho	48	Cb—
19	Ba I (R)—	82	Co—	49	Sm Nd—Sn
20	Ta	83	Ba—Eu	50	V I—
21	Ho—W Mn I	84	Lu Sm—	51	Fe I
22	Er	85	Dy Ti I—	52	Th—
23	Eu Y I—	86	Ni I—Co	54	Na I—Sn
24	Fe Ce—	87	Th—	57	Fe Nd
25	Mo	88	Y Dy—	58	Os Dy—
26	Pt Ir Sc I—	90	Cu V I (R)—	59	Sm—Rb I
27	Fe—	91	Ti I Sm—	60	Lu—Na I
29	Eu—	93	Co I—	61	Pr Ca I—
30	Mo I	97	Sb I	62	Ca I (R) Os—
31	Nd Cd I—	98	Ce—Ti	63	Ni—Ca I
33	Nd—	99	Th Cd I Eu—	64	Cb—U
34	Cs I Nd—	6100	La—Co	65	Fe—Dy La (R) Pr
36	Ir	01	Mo	66	Ca I—
37	Sn	02	Fe—Rh Cr Ca I (R)	68	Dy—
38	La (R) Tb	03	Zn II Li I (R)	69	Ca I—Ca I
39	V I	04	Tb—Lu Th	70	Er V I Nd—Pd
41	Lu	05	Co—	71	Sm—U
43	Ce—	06	Tb—	72	Pt U
44	Th—Eu	07	Co	73	Eu Fe I—
45	Sm Ta Sm—Cb	08	Ni I Eu Nd La (R)—	75	Ni I—
46	Pr	10	Pb Ir Sm Ba I (R)	76	Pd—Ni
47	Ta—	11	Ni—Cd I V I La (R)	78	Nd Eu
49	Co—Eu	12	Th	80	Gd—
51	U	13	Dy	81	Co I—
53	Ni I	14	Gd—Sm	82	Th
54	Sn	16	Cd I Ni I—Ru Co I	83	Zn
55	Lu Pr—Fe	18	Eu	85	Hf—
56	Cb	19	V I (R) Cu	86	Co—Ni I Rh
57	Ce	20	Th	88	Pd Eu—Co I
58	V I—	21	Zr	91	Ni I—Fe Ho Y I
				93	Co

Intensity (Ba 10 to 8; Ce 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
6195	<i>Eu Lu</i> —	6259	<i>Dy</i> —	6319	<i>Rh</i>
96	<i>Dy</i> —	60	<i>Dy</i> —	20	<i>Co La</i> (R)— <i>Si</i>
99	<i>O I Ru Ru—Lu Rh</i>	61	<i>Th Ti I Cr</i> —	22	<i>Fe</i>
6200	<i>Fe Ra</i> —	62	<i>Sc Eu La</i> (R)— <i>Er</i>	25	<i>Ta Cd I Cu—La</i> (R)
02	<i>Cr</i>	65	<i>Fe I—Mn</i>	26	<i>Er—V Pt</i>
03	<i>W Sn</i>	66	<i>La</i> —	27	<i>Cr—Sm Ni I</i>
04	<i>Ni I</i>	67	<i>Sm</i> —	29	<i>Cd I</i>
06	<i>Rb I</i> —	68	<i>Cu—Ta V I</i>	30	<i>Cr I—Ru</i>
09	<i>Ce</i> —	69	<i>Os</i> —	31	<i>Tb</i>
10	<i>Sc I</i>	71	<i>Dy Co</i> —	32	<i>Sb Th</i> —
11	<i>Co Ir—V</i>	72	<i>Ce</i> —	33	<i>Rb Sb</i> —
12	<i>Dy</i>	73	<i>Co</i> —	34	<i>Ir—Tb</i>
13	<i>Cs I Cb Fe I—V I</i>	74	<i>Th—V I Eu</i>	35	<i>Fe I—Eu</i>
14	<i>Sb—Zn II</i>	75	<i>Co</i> —	36	<i>Ti I—Fe I</i>
15	<i>Fe Ti I U</i> —	76	<i>Sc I—Co I</i>	39	<i>Ni I Zn</i> —
16	<i>Pt V I</i> —	77	<i>Rh</i>	40	<i>Sm—Co</i>
17	<i>Cs I</i>	78	<i>Au I</i> —	41	<i>Nd—Ba I</i> (R)
19	<i>Fe I—V</i> (R)	79	<i>Sc II</i>	42	<i>Th</i>
20	<i>Ti I</i> —	80	<i>U—Fe I</i>	43	<i>Dy—Ce</i>
21	<i>Er Sb—Lu Cb</i>	81	<i>Ta Pr</i> —	44	<i>Mn Fe</i> —
22	<i>Y I</i>	82	<i>Co I</i>	45	<i>Zr Lu—Sr I Sb</i>
23	<i>Nd Co I—Ni I</i>	83	<i>Pt</i>	47	<i>Gd Er—Co</i>
24	<i>V I</i>	84	<i>Se I</i> —	48	<i>Th</i>
25	<i>Ru</i> —	85	<i>V I—W</i>	50	<i>Eu</i> —
27	<i>Os</i>	88	<i>Ir—Pt</i>	51	<i>Pr Co</i> —
28	<i>Lu—Ce</i>	89	<i>Gd</i>	54	<i>Ho—Cs I Lu</i>
30	<i>Fe V I</i>	90	<i>Fe</i>	55	<i>Fe—Eu</i>
31	<i>Co I</i> —	91	<i>Eu—Dy</i>	56	<i>Ta</i> —
32	<i>Co Ce</i> —	92	<i>W Tb—V I</i>	57	<i>Mo Sm</i> —
33	<i>V I—Eu</i>	93	<i>Sc U—La</i> (R)	58	<i>La—Th Fe I</i>
34	<i>Ho Hg I</i> —	94	<i>Sm</i>	59	<i>Pr U</i> —
35	<i>Ba Lu Pb</i> —	95	<i>Ru—Ce</i>	60	<i>Ni I Ta</i>
37	<i>Sm</i>	96	<i>La</i> (R)— <i>V I</i>	61	<i>Nd</i> —
38	<i>Zn I</i> —	97	<i>Fe I</i>	62	<i>Nd Zn I—Cr I</i>
39	<i>Zn I—Sc I</i>	98	<i>Rb I U</i>	63	<i>Sr I</i>
42	<i>Lu—V I</i>	99	<i>Er—Zr Eu</i>	65	<i>Lu</i>
43	<i>Cu V I</i> —	6300	<i>Ce—Sc II</i>	66	<i>Ti I Ni I</i> —
44	<i>Nd</i> —	01	<i>Fe I</i>	68	<i>Sm</i> —
45	<i>Sc II</i>	02	<i>Fe I</i>	69	<i>Eu—Sr I</i>
46	<i>Fe I—Sm</i>	03	<i>W Eu—Ti I Tb</i>	71	<i>Ce</i> —
47	<i>Co</i> —	04	<i>Th</i> —	72	<i>U—Ho</i>
48	<i>Lu</i>	05	<i>Gd Ho—Sc I</i> (d)	76	<i>Ru—Th</i>
49	<i>Co La</i> (R) <i>Sc</i>	07	<i>Sm</i> —	78	<i>Ni I—U Sc I Mn</i>
51	<i>Cb V I</i>	08	<i>Er</i>	79	<i>U</i>
52	<i>Fe</i>	09	<i>Ta</i>	80	<i>Sr I Fe</i>
53	<i>Rh</i>	10	<i>Ce—Nd La</i>	81	<i>Gd</i> —
54	<i>Fe</i> —	11	<i>Co</i> —	82	<i>Nd Mn—Eu</i>
55	<i>Ho</i>	13	<i>Zr Co</i> —	83	<i>Eu</i>
56	<i>Fe Ni I—Ta Sm V I</i>	14	<i>Co—Ni I</i>	84	<i>Mn Ni I</i>
57	<i>Zr—Co</i>	15	<i>Fe</i> —	85	<i>Nd</i> —
58	<i>Ti I—V I Nd Ti I Sc I</i>	18	<i>Fe Pt—Mg I</i>	86	<i>Hf—Sr I Co I Sm Dy</i>
				88	<i>Er Sr I Sb</i> —

Intensity (*Ba* 10 to 8; *Cs* 7 to 5; *Sn* 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
6389	Ta— <i>U Sm Nd</i>	6455	Co <i>Ir—Pr Ca</i>	6525	Sc
90	Ru La(R)— <i>Sm</i>	56	La(R)—	26	La
91	Mo—	57	Th—Eu	27	Ba I (R) <i>Pr—</i>
92	Sb <i>Th Ta—U</i>	58	Ce—	28	Ru
93	Ce <i>Pr—Fe</i>	62	Co Ca I (R) <i>Th Fe I</i>	29	Cr—
94	La(R)—	63	Co Lu—	31	Th V I—
95	Co U—	65	U— <i>Sr</i>	32	W—Ni I
96	Th—Co I Dy Ga	66	Ce	37	Cr
97	U—	67	Ce— <i>Pr</i>	38	W <i>Gd Os—Y</i>
99	La—	69	Fe—	39	W— <i>Nd</i>
		70	Zr—	40	Ru— <i>Pr</i>
6400	Fe I—	71	Zn Mo—Ca I Ho	42	Sm
01	Mo—Eu	72	Sm—	43	U La—
02	Y I Dy—	73	Ce	44	Cb
03	Th Os—	74	Mo Cu—Co	46	Fe Ti I—Mo Mg II
04	W—Ni	75	Pr— <i>Fe Bi</i>		Sr
05	Tb	76	Bi I—	50	Ti I Sr—Ho Cu
06	Eu—	77	Lu Co	51	Co—
08	Fe I Sr—	78	Pr—	54	Ti I—
10	Eu Th—La	79	Zn I—	55	U— <i>Ce</i>
11	Pr Cu—U Fe I Th	81	Fe	56	Ti I—
13	Sc I—Th Er Ca	82	Ni Ni I Ba(R)	57	Y I—
	Ga(R) <i>Mn</i>	83	Eu— <i>Dy</i>	58	Sc Sb—
14	Ni I Rh	84	Sm Ni I	60	Th—
16	Th—	85	Cu Ta—Nd Mo	63	W Co—
17	Sm Ru Co	86	Pr Dy	64	Pr <i>Gd</i>
21	Cr Fe Ir Ni—Co I	87	Ra— <i>Sm</i>	65	Cu
	Dy	89	Zr	66	Pr
24	Mo Tb—Th	90	Sb Co— <i>Sm</i>	67	Eu
26	Sm	91	Mn Pr	69	Fe— <i>Sm</i>
28	Cr Ru—Ta Nd	93	Co Ca I	70	Sm <i>Mn</i>
29	Pr Co	94	Fe	72	Nd Ca I Cr I
30	Co I—Cb Ta Fe I	96	Ru—Ba II (R)	73	W
31	Pr	97	Bi	74	Ta
32	Nd	98	Sm Ba I (R)	75	Fe—
33	Cb—	99	La—Ca I	76	Os
35	Y I—			77	Th
37	Eu	6500	Pr	78	La
38	Te Cd I—	01	Cr I—Eu	79	Co Dy—
39	Ca I (R) Co Th—	03	Zr—Th U	80	Nd
40	Mn	04	Sr V I Co—	81	Tb
41	Lu Cr—Ni	05	Ta	83	Er—
43	Mn	06	Zr—	84	Th—
44	Pr—Co Ru Lu	08	Pd— <i>Co</i>	85	Sm— <i>Nd</i>
45	W—Zr Nd	10	Rh—	86	Ni I— <i>Cs</i>
46	Ra Mo—La Sr Tb	13	Ce	87	Cs I—
49	U—Co Ca	14	Ta—	89	Sm
50	Co I Ta—Ba I	16	Cr Ta—	91	Zr—
51	Co I—	17	Sb—	92	Ni I—Fe
52	V I—	18	Fe—	93	La—Ru Eu Th
53	Sn	19	Mn—Eu Rh Mo	94	Cr
54	La Sb	23	Lu Pt—	95	Ba I (R) <i>Pr—Co</i>

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLES AND CHARTS

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
6596	<i>Ru</i>	6672	<i>Cu</i> —	6750	<i>Fe</i> —
97	<i>Cr</i>	73	<i>Pr Ta</i>	51	<i>Cr</i> —
98	<i>Ni I</i>	75	<i>Ba I (R)</i> — <i>Ta</i>	52	<i>Rh</i> — <i>Gd Zr Fe</i>
99	<i>Ti I</i> — <i>Cu</i>	77	<i>Cb</i> — <i>Tb Fe</i>	53	<i>V La</i> —
		78	<i>W</i> — <i>Co I</i>	54	<i>Mo</i> —
6601	<i>Er</i> — <i>Sm</i>	79	<i>Sm</i> —	56	<i>Th</i> —
03	<i>Zr</i> —	81	<i>Gd</i> — <i>Sm</i>	59	<i>Er</i>
04	<i>Sm Sc Ho</i>	85	<i>Eu</i> —	60	<i>Pt</i> —
05	<i>Th</i> — <i>Mn V I</i>	86	<i>Ir</i> —	62	<i>Y Zr Cr</i> —
06	<i>Ce</i>	87	<i>Y I</i>	65	<i>Dy</i>
07	<i>Tb</i> —	90	<i>Ru Mo</i> —	66	<i>V</i> — <i>Ru</i>
09	<i>Fe</i> — <i>Pr</i>	93	<i>W Tb</i> — <i>Sm Ba I (R)</i>	67	<i>Ni I</i>
11	<i>Mo Sb</i> — <i>W Ta</i>		<i>Eu</i>	69	<i>Zr</i> —
12	<i>Cr</i> —	94	<i>Ho</i> —	71	<i>Co I</i> — <i>Ba</i>
13	<i>Y II</i>	96	<i>Al I</i> —	72	<i>Ni I</i> —
16	<i>La Er Pr</i>	98	<i>Al I</i>	74	<i>Ce La</i> — <i>Pd Ru</i>
17	<i>Sr Co</i> —			77	<i>Lu</i> — <i>Cd I</i>
18	<i>Nd</i>	6700	<i>Ce Y</i>	78	<i>Sm Sb</i> — <i>Sm</i>
19	<i>Mo I</i> — <i>Th</i>	02	<i>Tb</i>	79	<i>Zn</i> —
21	<i>Ta</i> — <i>Cu W</i>	04	<i>Ce</i> —	82	<i>Eu Sm</i>
23	<i>Co</i>	07	<i>Co Li I (R) Zr</i>	84	<i>Pd Co I</i>
24	<i>Ir V I</i>	09	<i>La</i>	85	<i>V Tb Pr</i> —
27	<i>Rh</i>	10	<i>Pt</i> —	89	<i>Hf</i> —
28	<i>Ce Ho</i>	11	<i>Lu</i> — <i>Lu</i>	90	<i>Sm Nd</i> —
30	<i>Cr I Rh Nd</i> —	13	<i>Y</i> —	91	<i>Sr I</i> — <i>Os</i>
32	<i>Sm Co</i> —	14	<i>Tl I</i> —	93	<i>Y I Lu</i>
34	<i>Gd</i> —	15	<i>Cr</i> —	94	<i>Sm</i> — <i>Tb</i>
35	<i>Ni</i> —	16	<i>Hg I</i> —	95	<i>Y II</i> —
36	<i>Y</i> —	17	<i>Ca I</i>	96	<i>Rh</i>
37	<i>Nd</i>	18	<i>Ru</i> —	98	<i>Pr</i>
43	<i>Dy</i> — <i>Sr Ni I</i>	21	<i>Er</i>		
44	<i>Hf Th N I</i>	23	<i>Sm Cs I (R) Cb</i>	6802	<i>Eu</i>
45	<i>Eu</i> —	24	<i>Sm</i>	04	<i>Nd</i> —
48	<i>Pt</i> —	25	<i>Sm</i>	06	<i>Sb</i> — <i>Os</i>
49	<i>Ru</i>	26	<i>Fe U</i>	09	<i>Co I</i> —
50	<i>Mo</i> — <i>Nd U La</i>	27	<i>Th</i>	10	<i>Fe</i> —
52	<i>Ce</i>	29	<i>Os Cr</i>	12	<i>V</i> —
54	<i>Ba</i> —	30	<i>Gd</i>	13	<i>Ta</i> —
55	<i>Nd</i>	31	<i>Sm</i>	14	<i>W Co I</i>
56	<i>Pr</i>	34	<i>Mo I Sm Cr</i> — <i>Sm</i>	16	<i>Eu</i> —
58	<i>Dy</i> —	35	<i>Y</i>	17	<i>Sc</i> —
59	<i>Mo</i>	36	<i>Pr</i>	19	<i>Hf</i> — <i>Sc</i>
60	<i>Pb</i> —	37	<i>Nd Sc</i>	20	<i>W</i> —
61	<i>Cr La</i> — <i>Dy</i>	38	<i>Sb</i>	23	<i>La</i>
62	<i>Th</i> —	39	<i>Sc</i>	24	<i>Ru</i> —
63	<i>Ru Fe</i> —	40	<i>Nd</i> —	25	<i>Er</i> —
64	<i>Y</i> —	41	<i>Cu</i> —	26	<i>U</i>
65	<i>Ce</i>	43	<i>Ti I</i> —	27	<i>Pr</i>
67	<i>Ir Dy</i>	44	<i>Eu</i>	28	<i>Cb Gd</i> — <i>Fe</i>
68	<i>Ir</i> —	46	<i>Mo Mo</i> —	29	<i>Mo</i> — <i>Sc Sm</i>
69	<i>Cr</i> —	47	<i>Pr</i> — <i>Dy</i>	30	<i>Ir</i> — <i>Pr</i>
71	<i>La</i> — <i>Sm</i>	49	<i>Pr Cu</i> —	32	<i>Y Zr</i>

Intensity (*Ba* 10 to 8; *Cs* 7 to 5; *Sm* 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
6533	Pd—	6907	Hg I—	6994	Zr Er—
35	Sc—Dy	08	Co Y W—	95	Sb
38	Mo	11	K I Ru—	96	Gd
41	Fe—V	14	Mo—Ni I	97	Co—
42	Ni I—Pt	16	Pd Gd Tb Fe	99	Ce Fe I
43	Fe	17	Lu—		
44	Sn—Sm	20	Cu—Gd	7000	Gd
45	Y—	23	Tb Ru—	01	Er—Rh Ni I Mo
46	Sm—Gd Nd Zr	24	Cr I—Ce Gd	04	Co I
47	In I	25	Cr I La—	05	Tb
48	Er Sm—Mo	26	Er—	06	Gd—
50	Pr	28	Zn I—	08	Y
53	Dy Y—	29	Ir	09	Y
55	Fe—	31	Mn—	16	Fe Pd—Co I
56	Sm—	34	W—La	17	Dy—
57	Gd—	35	Cu	20	Sm—
58	Fe Co—	37	Co	21	Pr
61	Sm Ti I—	38	Er—Zn I	22	Fe I
62	Sm	39	K I—	24	Ni I
64	Ta—Eu	41	Nd—	26	Y—
65	Ba	42	Mn Pt	27	Co Ru
66	Ta—	43	Zn I—Th	30	Ni I—Ce
67	Ba—	44	Er	31	Lu—
70	Co I	45	Fe—Gd	32	Co
71	V	50	Sm Y	34	Ni—
72	Co Sm—	51	Fe—Y Er	35	Y—
74	Tb—	53	Ir	36	Bi—
75	Ta—	55	Ni I Sm—Cs Os	37	Gd Nd—Ir Mo
78	Sr I—	57	Gd	38	Fe I—Ti
79	Rh	58	Y La—	39	Sm Cu—
80	Er—	59	Gd—	40	Eu—
81	Pr—Cr I Cu	64	W—	42	Sm Pr—
82	Cr I—	65	Ni—Rh	45	Gd Mo—Th
83	Cr I—Mo	66	Ta—Zr	46	Cb
85	Sm—Fe	71	Gd	50	Gd
86	Mo—	73	Cs I (R)—	51	Pr—Sm
87	Y—Gd Mn Rh	74	V	52	Co I Y
88	Zr—	76	Gd	54	Co—Gd
89	Th—Cu	78	Gd—Cr Fe	55	Dy
90	Cu	79	Rh—Cr I Y	58	Gd—
92	Mo—Sr I Pr	80	Pr—Gd Cr I Ce	59	Ba(R)
93	Ir—	81	Cr I—	60	Pd—Os
95	U	82	Ru—	61	Ce
96	Tb—	83	Cs I—	63	Ni I—
97	Er	84	W—Os	66	La—Nd
98	Ce—	85	Gd	68	Gd La Fe—
99	Ce Dy—Tb	86	Ce—	69	Mn Gd
		88	Gd	70	Sr I Co—Gd
6900	In I Nd—Gd	89	Mo—Th Mn	73	Gd
02	Tb—	90	Zr	74	U
03	Eu	91	Bi—Gd	75	Dy—
05	Cu	93	Th—	77	Gd Eu—

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
7080	<i>Pr</i> —	7164	<i>Fe I</i> —	7252	<i>Cs Gd</i>
82	<i>Hg I Sn</i> —	65	<i>Lu</i>	53	<i>Os</i>
84	<i>Tb Co I</i>	67	<i>Ni I Sr I</i> —	61	<i>Ni I</i>
85	<i>Gd</i>	68	<i>Gd</i> —	62	<i>Gd</i>
86	<i>Ru Ce</i> —	69	<i>Zr I</i> —	63	<i>Nd—Gd</i>
87	<i>Ru</i> —	70	<i>La</i> —	64	<i>Y Zn V—Zr</i>
89	<i>Ba</i>	72	<i>Gd</i> —	66	<i>Ni</i> —
90	<i>Fe I</i> —	75	<i>Eu</i>	67	<i>Mo I</i>
91	<i>Hg I</i>	82	<i>Ni I</i> —	68	<i>Rh</i> —
94	<i>Co Pt</i>	83	<i>Ir</i>	69	<i>W</i>
95	<i>Ni—Zr</i>	84	<i>Mn</i> —	70	<i>La—Cs Rh</i>
97	<i>Zr I</i>	85	<i>Cr</i>	74	<i>Gd</i> —
98	<i>Gd</i> —	87	<i>Fe I</i> —	78	<i>W</i> —
		89	<i>Nd—Gd</i>	79	<i>Gd</i> —
7101	<i>U Rh Gd</i>	91	<i>Y</i>	80	<i>Cs II Rb I Zr</i>
02	<i>Co Zr I</i>	92	<i>Nd</i> —		<i>Ba(R)</i> —
03	<i>Zr I</i>	93	<i>Cu Co</i>	82	<i>La</i> —
04	<i>Rh</i> —	94	<i>Eu Gd</i>	83	<i>Mn I</i>
06	<i>Eu</i> —	95	<i>Ba I—Y</i>	85	<i>Nd Co—W</i>
09	<i>Dy—Mo I</i>	97	<i>Ni I</i> —	88	<i>Nd Fe I</i>
10	<i>Ni I</i>			91	<i>Ni I Gd</i> —
11	<i>Zr</i>	7200	<i>W</i> —	93	<i>Fe I</i> —
13	<i>Co Pt</i>	01	<i>Gd</i> —	96	<i>W</i>
14	<i>Pr</i>	02	<i>Ca</i> —	98	<i>Nd</i>
16	<i>Pd Gd</i>	04	<i>Tb</i> —		
18	<i>Gd</i>	06	<i>Os</i> —	7300	<i>Mo</i> —
20	<i>Ba</i> —	07	<i>Fe I</i> —	01	<i>Eu Gd</i> —
22	<i>Ni I—Gd Mo</i>	08	<i>Pr</i>	02	<i>Mn I</i>
24	<i>Co</i> —	09	<i>Ti I</i> —	09	<i>Sr I</i> —
25	<i>Lu</i>	16	<i>Ti W</i> —	13	<i>Gd</i> —
28	<i>Y—U</i>	17	<i>Eu Pt</i>	15	<i>Co</i>
29	<i>Nd</i> —	19	<i>Cs</i>	16	<i>Er—Nd</i>
30	<i>Fe I</i>	21	<i>Lu</i> —	18	<i>Zr</i> —
31	<i>Hf</i>	22	<i>Sb</i>	23	<i>Nd</i> —
32	<i>Cd I</i> —	23	<i>Fe</i>	24	<i>Gd</i>
33	<i>Gd</i> —	26	<i>W</i> —	26	<i>W Ca I—Mn I</i>
34	<i>Mo I Co</i> —	27	<i>Pr</i>	27	<i>Ni I</i>
35	<i>Er</i>	28	<i>Ba Pb</i>	29	<i>Ce</i>
39	<i>Y</i>	29	<i>Cs I</i> —	30	<i>Pb</i> —
40	<i>W</i>	32	<i>Sr I</i> —	34	<i>La</i> —
45	<i>Os</i>	33	<i>Gd</i> —	38	<i>V</i>
47	<i>Gd</i> —	34	<i>Co</i> —	44	<i>Ti I</i>
48	<i>Ca—Os</i>	36	<i>Nd</i>	45	<i>La</i> —
49	<i>Pd—Sm</i>	37	<i>W—Lu</i>	46	<i>Y</i> —
50	<i>Ce</i> —	38	<i>Ce—Ru</i>	48	<i>Mo</i> —
51	<i>Mn</i> —	39	<i>Fe I</i>	54	<i>Co I</i>
53	<i>Sr—Ba</i>	42	<i>Gd—Mo I</i>	55	<i>Cr I (R)</i>
54	<i>Co I</i>	44	<i>Ti I</i>	56	<i>V</i> —
58	<i>La</i> —	45	<i>Mo</i>	59	<i>Ba</i> —
59	<i>Co Mo Zr</i>	47	<i>Mn</i>	61	<i>Mo</i>
61	<i>La</i> —	50	<i>Co</i> —	63	<i>V</i> —
62	<i>W</i>	51	<i>Os—Ti I</i>	64	<i>Ti I</i> —

Intensity (*Ba* 10 to 8; *Cs* 7 to 5; *Sn* 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)

PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
7363	Pd—	7485	Mo I Ru	7601	Mo
70	<i>Eu Ho</i> —	86	Pd	02	Os
77	Gd—	88	Ba Gd—	03	Mn—
81	W—Ni	89	Co—	09	Cs I—
82	Cd I—	90	Er—	10	Ca Ni Co Ba—
85	W Ni Cd I—	95	Fe I Rh—Pr	12	W—
86	Gd Ni Fe—	98	La	14	W—
88	Co	99	Pr—Ru	17	Ni I—
89	Fe I—			19	Rb I Ni I U—
91	Mo I—Pd	7503	Bi—	20	Fe
92	Ba I—	04	W Mo—	21	Ru Sr I Gd
93	Ni I Ru	08	W	24	Zn
94	Gd	10	Au I	26	Pr—
97	Ce	11	Fe I Nd—	31	U
99	Gd I—	13	Nd	34	Co
		15	Mn	36	Ba
7400	Cr I—	16	Nd—Dy	37	Co
01	Ni—	22	Ni I	39	Nd
05	Sb	25	Ni I—	41	Dy—
06	Nd	28	Ba—	42	Ba
07	Os	29	Nd—	45	Pr Dy
08	Rb I—	31	Fe—	46	Mn—Dy
09	Ni I—	33	Co U	48	Co Sb—
11	Fe I—	37	W—	50	Gd—
12	Dy—	38	Nd—	51	Mn
14	Ni I	39	La—	54	Ni Er—
17	Co I—Ba	41	Pr—	56	Mo
18	Nd—	43	Dy	57	Mg I
22	Ni I—	47	Nd—	62	Dy—
25	U	50	W—	64	La—Zn K I (R)
26	Gd—Dy	51	Mn—Mn	69	U
34	Mo—	53	Dy—	70	Mn—
37	Co I—	54	Co—	72	Ba—Gd
40	Ti I	55	Ni I	73	Sr—
41	Bi—	57	Rh	79	Mo
42	Gd Rh—	59	Ru Dy	80	Er Mn—
45	Fe I	61	Co—	87	Ag I
47	Mo—	62	Dy	88	W
48	Nd	63	Gd Y	89	Ce—
50	Y—	64	Co	90	Rh
51	W—Pr	66	U—	96	Nd
52	Mo	68	Fe I	98	Zn
57	Co—	69	W	99	Nd K I (R)—
59	Ba	70	Cu—		
62	Cr I—	72	Mo	7700	Pb—W
64	Gd—	74	Ni I—	04	Pr
68	Ru	77	Rh—	06	Ba Mn
69	Er—	78	Zn	09	Mo
75	Rh	82	W	10	Mn—
78	Zn II	86	Fe—Co	12	Mn—Co
81	Cb Ni—	90	Co	14	Ni I—Pr
83	W La—	95	Mo—	15	Dy—Ni I

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE III (Continued)
PRINCIPAL LINES BY WAVELENGTH

Wave-length	Elements	Wave-length	Elements	Wave-length	Elements
7719	Y	7800	Rb I (R)—	7881	Ru—Y U
20	Mo	05	Mn	86	W—
21	Pr	08	Cr—Nd W	87	Mo
22	Ru	09	Ru—	90	Ni I—
23	Cr—Mo	12	Dy—		
24	Y—	16	Mn Sb	7905	W—Ba I
27	Ni I	21	Mn—	06	Sb
29	Hg—Dy	24	Rh	08	Cr—Co
32	Mo—	26	Ni I	09	W Dy—
33	Mn—Gd	29	Mo	11	Ba I—
34	Co Mn—	30	Rh—	15	Pd
43	Co—	32	Fe—	17	Ni I—
48	Fe—Ni	34	Mn Ir—	23	Mo—
49	Gd—	35	Ce	24	Ru—Sb
50	Nd	36	Al I	26	Co
51	Ba	37	Sb—	30	Gd—
52	Mn	38	Co—Bi	32	Zn
54	Sn	39	Ba	33	Cu I—
55	Mn—Sb	40	Co Bi—	37	Fe I—Zn
57	Rb I	42	Cr—	42	Cr—Mn
59	Rb I	44	Sb—	44	Cs I—
61	W—U	46	Gd—	45	Fe
63	Pd	47	Ru	47	Rb I (R)
64	Mn Sb	52	Os—	49	Ti I—
66	Ba I	54	Mo—	57	W—Co
71	Fe	55	Co	58	Nd
72	Rh	56	Gd	61	Ti
73	Nd—	59	Ce Ni—	65	Nd
76	W	60	Ce	69	Sb—
80	Ba Fe	61	Ni I—	70	U—
84	W U—	62	Nd	78	Ti I
86	Pr—Pd	63	W—Ni I	86	Mo
88	Ni I	67	W Sb—	87	Co—
90	Os Dy—Mn	69	Co	94	Ni
91	Rh Ru	71	Co—Pr	96	Ti—
97	Ni I Ce	78	Ba—	98	Fe I
99	Zn I—	80	W—		

Intensity (Ba 10 to 8; Cs 7 to 5; Sn 4 to 2). (—) = 0.5A; no dash indicates greater than 0.5A.

TABLE IV
PRINCIPAL LINES BY ELEMENTS

(A40, A36, A22, A18, A19, A61, A52, A64)

I, II, and III indicate ionization states, R indicates reversal p indicates persistent line. Symbols after the wavelength indicate lines used for qualitative and quantitative analysis and refer to the control lines listed with the same element. Interfering lines are those which may cause trouble if present in the sample. No wavelength values are given for these lines, but they can easily be determined by checking the lines of the interfering element for a wavelength value approximately the same as the line of the element to be identified.

Qualitative Analysis		Quantitative Analysis	
*, †, ‡, §, , ¶, ** = Gerlach and Riedl (A19).		G = Gerlach (A18, A19a and other publications).	
Quantitative Analysis		N = Smith (A63 and other publications).	
L = Lundegardh (spark) (A52).		B = Brode (C19, C31 and other publications).	
F = Lundegardh (flame) (A52).		M = Duffendack, Owens, Sawyer (C42, C47 and other publications).	
S = Scheibe (A59 and other publications).			

Subaunbers, S₂, B₂, etc., indicate pair combinations of unknown and control lines. Arc and spark intensities are given from 1 to 10.

The symbols (+) and (°) in front of the wavelength value (see iron table) indicate secondary and tertiary standards, respectively.

For more complete information on control and interfering lines one should consult Gerlach and Riedl, "Tabellen zur qualitativen Analyse, Die chemische Emissionsspektalanalyse," Vol. III (A19), and the literature publications of Duffendack, Scheibe, Gerlach, Smith, Lundegardh, Brode, and others.

More complete information on the lines of elements, arranged according to element, including those elements and lines omitted from these tables can be found in Kayser (A40), International Critical Tables (A36), (A22), and other sources indicated in Chapter IV (page 63).

ALUMINUM

Al

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
II 2 094.8	5	II 2 669.2	10	I 3 961.5p§LB ₂	10R	8R
I 2 168.0	1R	1	III 2 762.8	9	II 4 226.8	6
I 2 174.0	1R	1	II 2 816.3	10	III 4 480.0	5
I 2 263.5	4R	2R	III 2 907.5	10	III 4 512.3	5
I 2 269.1	4R	2R	II 3 050.1	4	8	III 4 529.2	6
II 2 321.6	2	6	3 054.7	4	2	II 4 585.8	6
I 2 367.1	8R	4R	II 3 057.2	4	10	II 4 663.1	10
II 2 369.3	1	4	3 064.3	4	2	III 4 701.7	6
I 2 372.1	3	3	3 066.2	4	2	III 5 150.9	5
I 2 373.1	8R	4R	I 3 082.2p*S ₁	10R	8R	III 5 163.9	7
I 2 373.4	2R	2R	I 3 092.7p†	10R	8R	II 5 593.2	10
I 2 378.4	3	1	I 3 092.9S ₂	6R	4R	III 5 696.5	5
II 2 545.6	6	II 3 443.7	6	III 5 722.7	6
II 2 568.0	10R	6R	II 3 587.1	10	II 5 861.5	7
I 2 575.1	10R	6R	III 3 601.6	7	II 6 231.8	7
I 2 575.4	3R	2	III 3 612.4	7	II 6 243.4	10
II 2 631.7	7	II 3 655.0	8	I 6 696.1	3
I 2 652.5	10R	4R	I 3 944.0p†LS ₂	10R	8R	I 6 698.7	3
I 2 660.4	10R	5R	B ₁					

Control lines: *Fe 3075.7
†Fe 3222.1
‡Ti 3981.8
§Co 3917.1
Cr 3919.2

Interfering lines: *Au Cd Co Mo V W
†Au Fe Mg Mo V
‡Ba Co Fe Mo Ni V W
§Ca Co Fe Mo Ni Sr Sb W

Control lines: B₁Ca 3933.7
B₂Ca 3968.5
SiCu 3128.7
S₂Cu 3094.0
S₂Cu 4022.7

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

ANTIMONY

Sb

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 023.9	4	2 718.9	3R	10	I 4 033.5	6	4
2 039.7	5	2 727.2	5R	8	4 195.1	8
2 054.0	6	I 2 770.0N ₂	10R	10R	4 265.0	10
I 2 175.9p	5R	3R	2 790.4	10	4 352.2	10
2 179.3	4R	3R	2 851.1	4	4	4 591.8	5
2 306.5S ₁	5R	4	I 2 877.9§N ₂	10R	10R	4 693.0	10
I 2 311.5p*§S ₂ N ₁	6R	10R	2 913.3	5	5 568.0	3	3
2 373.7	4R	3	I 3 029.8S ₂ N ₂	8R	10	5 632.0	4
2 383.6S ₂	3R	4	3 040.7S ₂	10	5 639.7	2	5
I 2 445.6	3R	6	I 3 232.5pS ₁₀ N ₂	8R	10	5 730.4	4
I 2 528.5†S ₂ N ₂	6R	10R	3 241.2	10	6 005.0	6	3
2 590.3	10	I 3 267.5pB	8R	10	6 079.6	6	1
I 2 598.1p†S ₂ N ₂	10R	10R	I 3 383.2	5	2	6 129.9	6	3
2 612.3	3R	8	3 473.9	10	6 611.4	3	2
2 652.6	3R	8	3 498.5	10	6 778.4	6
I 2 670.7S ₂ N ₂	5R	5	I 3 504.5	3	10	6 806.3	6	1
2 682.8	4R	5	I 3 637.8	9	6	7 844.4	4
2 692.3S ₇	3R	3	I 3 722.8	8	5	7 924.6	6

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Cd 2144.4	*Co Fe Mo V	‡Fe 2483.3	‡Ag Pb Cr Fe Mn W
Co 2307.9		Fe 2611.9	
Ni 2320.1		§Cr 2865.1	§Cu Cr Ir Pd Pt V
†Co 2521.4	†Au Ba Pb Si Co Mo V W	Ga 2943.6	
Fe 2522.9		Si 2516.1	
Si 2506.9			
Control lines:	Control lines:	Control lines:	
B Cu 3274.0	NiSn 2359.7	NaSn 2637.0	
3268.3	2282.2	2504.4	
SiPb 2322.0	2333.0	2368.2	
S ₂ Pb 2399.6	2282.2	2558.1	
2388.8	Sn 2368.2	Sn 2571.6	
2332.5	2317.2	Pb 2657.2	
S ₂ Pb 2388.8	Pb 2399.6	2562.4	
SiPb 2657.2	2388.8	2628.3	
2562.4	2332.5	N ₂ Sn 2637.0	
S ₂ Pb 2657.2	N ₂ Sn 2523.9	Pb 2657.2	
2628.3	2455.9	N ₆ Sn 2761.8	
S ₂ Pb 2657.2	2433.5	Pb 2657.2	
S ₂ Pb 2657.2	2531.1	N ₆ Sn 2761.8	
S ₂ Pb 3043.9	2571.6	N ₇ Pb 3034.9	
S ₂ Pb 3043.9	Sn 2546.6	N ₂ Sn 3223.6	
SnPb 3220.5	Pb 2428.6	3218.7	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 ARSENIC
 As

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 031.	10	I 2 860.5†	4R	8	4 371.	5
2 074.	12	I 2 898.7	4R	6	4 431.6	4
2 113.	2	3	2 959.6	7	4 474.4	4
2 134.	2	2	I 2 991.0	2	4	4 494.4	3
2 144.2	4	1	I 3 032.8	4	8	4 530.8	3
2 165.5	4	2	I 3 075.3	2	5	4 985.4	5
2 271.4	4	1	I 3 119.6	4	7	5 105.5	8
I 2 288.1p*LS ₁	10R	3	3 787.2	3	5 107.6	8
I 2 349.8p*LS ₂	10R	6	3 842.9	4	5 161.1	7
2 369.7	4R	5	3 922.5	10	5 331.3	8
2 370.8S ₂	4R	5	3 948.6	3	5 496.9	5
I 2 381.2	4R	5	4 006.2	3	5 497.8	10
2 437.2	1	5	4 037.0	6	5 558.1	10
2 456.5	4R	7	4 197.5	3	5 651.3	10
2 492.9	2	5	4 299.4	3	6 023.	6
I 2 745.0S ₁	6R	5	4 336.7	5	6 110.	6
I 2 780.2p†L	8R	10	4 352.1	5	6 170.	6
2 830.4	4						

Control lines:

*Be 3130.4

†Fe 2772.1

Mg 2802.7

Mg 2790.8

Mo 2775.4

†Cr 2865.1

Interfering lines:

*Be Fe Mo Ti V W

†Au Bi Cr Co Ga Mg Mn Mo

Pb Sn Ti Zn W

†Mo Pt Ti

Control Line

Cr 2858.7

Cr 2862.6

S₁Pb 2242.5

2332.5

S₂Pb 2332.5S₂Pb 2399.6S₁Pb 2628.3

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

BARIUM

Ba

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
II 2 304.2	6R	8R	II 4 166.0	5	10	II 5 853.7	8R	5
II 2 335.3	6R	10R	I 4 283.1	8	8	I 5 907.6	6	2
II 2 347.6	5	7	I 4 323.0	4	1	I 5 971.7	10	3
II 2 528.5	6	I 4 332.9	4	1	I 5 997.1	7R	3
I 2 596.7	6	4 350.4	8	5	I 6 019.5	7R	3
II 2 634.8	5	8	4 402.6	8	6	I 6 063.2	8R	4
II 2 647.3	4	4	I 4 431.9	7	6	I 6 110.8	8R	5
I 2 702.7	6	2	I 4 489.0	7	2	II 6 141.7	10R	10R
II 2 771.4	2	3	I 4 493.6	5	2	I 6 341.7	7R	3
I 2 785.3	6	4 505.9	8	5	I 6 450.9	7	3
I 3 071.6	8R	6R	4 523.3	8	3	6 482.9	7R	3
I 3 262.4	3R	II 4 525.0	8	10	II 6 496.9	10R	10R
I 3 356.9	6	II 4 554.0P*L	10R	10R	I 6 498.8	8R	4
I 3 377.0	8	4 573.9	6R	4	I 6 527.3	8R	3
I 3 377.4			4 579.7	8R	8	I 6 595.4	7R	3
I 3 420.3			4 599.8	6R	2	I 6 675.3	6R	2
I 3 421.0	10	I 4 620.0	5	1	I 6 693.9	6R	2
I 3 421.5			I 4 628.8	5	1	6 865.7	5
I 3 501.1	8R	2	I 4 673.6	7	2	I 7 060.0	8R
I 3 525.0	6	4 691.6	7R	4	II 7 120.3	6
I 3 544.7	6	I 4 700.5	6	1	I 7 195.3	6
I 3 547.7	4	I 4 726.5	8	5	7 228.8	5
I 3 579.7	6	2	II 4 900.0	8	10	7 280.3	8R
3 630.7	8	2	I 4 902.9	4	I 7 392.4	6
3 889.3	5	2	II 4 934.1p	10R	10R	7 417.6	4
II 3 891.8	8	8R	I 5 424.6p	7	3	7 459.7	5
3 892.7	5	I 5 519.1p	8R	5	7 488.1	5
I 3 909.9	6	6	I 5 535.5P†F	10R	6	7 642.9	5
I 3 935.7	7	6	5 680.2	5	1	7 672.1	7
I 3 937.9	5	3	I 5 777.7p	10R	5	7 780.5	8
I 3 993.4	8R	6	5 800.3	7	2	7 830.6	5
II 4 130.7	8R	10R	5 805.7	5R	2	I 7 905.8	7
4 132.4	5	3	I 5 826.3	4	7R	I 7 911.4	6

Control lines: Interfering lines:

*Be 4535.5 *Al Be Co Cr Cs Cu Fe Mn
 Mo 4558.5 Mo Ni Pb Pt Si Ti V W
 Ni 4551.3
 Ti 4552.5

Control lines:

†Mo 5506.5

Interfering lines:

†Al Be Bi Ca Co Cu Fe Mg
 Mn Mo Na Ni Pb Sb Sr
 Ti V W

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)

PRINCIPAL LINES BY ELEMENTS

BERYLLIUM

Be

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 056.7	4	I 2 651.0B ₁	10	10	I 3 322.0	8	2
I 2 175.7	10	II 3 047.9	4	I 3 322.3	8	2
2 348.6P*	8R	3	II 3 130.4†L	10	10R	II 4 362.2	7
I 2 351.5	6	II 3 131.3LB ₂	9	10	4 572.7	8	1
I 2 494.5	7	3	3 132.0B ₃	9	5	II 4 674.6	8
I 2 494.6	7	3	II 3 198.0	4	II 5 274.3	4
I 2 494.7	7	3	II 3 275.6	5			

Control lines:

Interfering lines:

Control lines:

*Fe 2364.8

*Al As Bi Fe Ni Os Pt

B₁Mn 2939.3

Fe 2358.6

B₂Bi 3067.7

†Cr 2849.8

†Ag Cr Hg Mn Os V W

B₃Bi 3067.7

Hg 3650.2

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

BISMUTH

Bi

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 061.7p	8R	3	2 696.8G ₂	6R	4R	4 302.1	10
2 110.3	8R	2	2 730.5S ₂ G ₃	5R	2R	4 308.2	4	2
2 133.6	7R	2 780.5pG ₄	7R	4	4 308.6	4	2
2 134.4	8R	1	2 809.6p	8R	2	4 340.6	4
2 143.6	2	2 898.0p*N ₂ G ₅	10R	5R	4 561.2	8
2 144.4	2	2 938.3pB ₁ S ₄ N ₂	10R	8R	4 722.2	10	5
2 152.9	7R	2 989.0pS ₂ N ₄	9R	5R	4 722.5N ₅	10	8
2 153.5	4R	2 993.3	9R	4	4 722.7	8	8
2 156.9	4R	3 024.6B ₂ S ₆ G ₆	8R	4R	5 124.4	4
2 164.1	4R	3 067.7P†LS ₇	9R	6R	5 144.5	6
2 177.3	6R	1	G ₇ N ₅			5 209.3	10
2 189.6	6R	3 397.2B ₃	5R	2	5 552.2	8	3
2 203.1	4	1	3 405.2	2R	1	5 742.6	6
2 228.3	6R	2R	3 510.9B ₄	6R	5	5 861.1	4
2 230.6S ₁	8R	4R	3 596.1	3R	4	6 128.1	4
2 276.6P	5R	2	3 695.5	8	6 134.9	5	1
2 309.3	4	3 792.9S ₅	8	6 497.5	4
2 400.9S ₂	8R	7	3 887.9	2	1	6 600.1	7
2 430.5	2	3 888.2	2	1	6 809.1	7
2 489.4	5	1	4 079.2	10	6 991.1	4
2 515.7	6R	1	4 121.5	6	4	7 838.7	3
2 524.5	7R	2	4 121.9S ₃	6	4	7 840.3	2
2 627.9G ₁ N ₁	8R	4	4 259.6	10	8 210.8	10

Control lines:

*As 2745.0
Mo 2911.9
V 2903.1
W 2947.0

Interfering lines:

*As Be Co Cr Ti V

Control lines:

†Fe 3057.5
Ti 3073.6
V 3073.8
V 3185.4

Interfering lines:

†Fe Mo V W

Control lines:

B₁Sn 2863.3
B₂Sn 2850.6
B₃Cu 4275.1
Pb 3683.5
B₄Pb 3739.9
S₁Pb 2253.9
S₂Pb 2400.9
S₃Pb 2657.2
S₄Pb 2926.8
S₅Pb 2980.3
S₆Pb 3220.5
3240.2
S₇Pb 3221.7
3119.1
3043.9
3040.2
2657.2
S₈Pb 3786.3
S₉Pb 4168.0
G₁Sn 2637.0
G₂Sn 2765.0

Control lines:

G₃Pb 2657.2
G₄Pb 2657.2
G₅Sn 3141.8
2863.3
G₆Pb 3220.5
G₇Sn 3009.1
3141.8
3218.7
3223.7
Pb 3220.5
N₁Sn 2637.0
N₂Sn 2850.6
2671.8
Pb 3043.9
2966.4
N₃Pb 3043.9
2966.4
N₄Sn 2896.0
2850.6
2761.8
Pb 3043.9

Control lines:

2980.2
2973.0
N₅Sn 3223.6
3218.7
3175.0
3141.8
3034.1
3009.1
2913.3
Pb 3262.4
3240.2
3220.5
3176.5
3043.9
3119.2
2980.2
2973.0
Cu 3140.3
3108.6
N₆Sn 4324.7

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

CADMIUM

Cd

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 004.2	5	I 3 080.8	S	3	4 094.8	4
2 062.0	5	3 095.5	5	4 127.0	4
II 2 144.4PN ₁	4R	6R	3 129.2	5n	II 4 134.8	15
II 2 194.6	1	4R	I 3 133.2	2	5	4 191.6	4
2 239.9	6R	3	3 185.5	5	4 216.9	6
II 2 265.0P*LN ₂	4R	10R	II 3 250.3	25	4 245.6	4
2 267.5	4R	2	I 3 252.5	8	6n	II 4 412.3	10
I 2 288.0P†LG ₁	10R	10R	I 3 261.1†	10R	7	4 415.7	1	6
N ₂			3 299.0	4	4R	I 4 678.2S ₄ N ₂	10	10
2 306.6	4R	3	I 3 403.7pG ₂ N ₂	10R	10	I 4 799.9[§S ₆ N ₂	10R	10
II 2 312.9S ₁ N ₄	4	10R	II 3 417.4	10	II 4 881.7	10
II 2 321.8N ₄	1	7	I 3 466.2pG ₂ N ₇	10R	8R	I 5 085.8S ₆	10R	10
2 329.3	8R	6	I 3 467.7G ₄	8R	10	II 5 337.5	3	25
2 409.8	4	II 3 495.4	15	5 338.5	10
I 2 553.6	4	II 3 535.7	20	II 5 378.1	10
II 2 673.0S ₂	4	10	I 3 610.5p§S ₃ G ₅	10R	10R	II 5 381.8	10
I 2 639.5	6R	1n	I 3 612.9	8R	9	5 497.0	10
I 2 677.6	8	3n	I 3 614.4G ₆	7	7	5 637.3	5
I 2 712.6	6	2n	I 3 729.1	4R	I 6 099.1	5
II 2 748.6	10	3 940.8	5	I 6 325.1	5	1
I 2 768.9	6R	3N	3 976.6	5	I 6 329.9	5
I 2 836.9	8R	6N	3 977.3	5	II 6 359.9	10
I 2 868.3	0	3	3 988.2	4	I 6 438.5	10	10R
I 2 880.8	8R	6	II 4 029.1	10	II 6 465.0	10
I 2 881.2	4R	3N	4 057.5	5	II 6 725.8	15
I 2 980.6	8R	6						

Control lines: *Al 2269.1
Ni 2270.4
†As 2349.8
†In 3256.1
Sn 3034.1
Ti 3242.0

Interfering lines: *Fe Os
†As Au Fe Mo
†Co Fe In Mo
V W

Control lines: §Fe 3618.8
Mo 3447.1
Ni 3510.3
||Os 4394.9

Interfering lines: §Al Ba Cr Cs Cu
Ni Pt Ti V
||Ag Al As Be Co
K Mo Ni Ra

Control lines:
S₁Pb 2322
S₂Pb 2657.6
2562.4
S₃Pb 3671.5
S₄Pb 5005.5
5042.8
S₅Pb 5005.5
5042.8
S₆Pb 5042.8
G₁Sn 2282
G₂Sn 3331
3656
3142
3219
G₃Sn 3656
3219
3224
G₄Sn 3656
3219

Control lines:
3224
G₅Sn 3656
G₆Sn 3656
N₁Sn 2199.3
N₂Sn 2282.2
2267.2
2268.9
2317.2
Pb 2243
2253.9
N₃Sn 2380.7
2333
2286.7
2231.7
2282.2
2286.7
Sn 2317.2
Pb 2332.5

Control lines:
2249
2243
3043.9
N₄Sn 2317.2
Pb 2332.5
N₅Sn 2251.2
N₆Sn 2223.6
3218.7
3352.3
3240.2
N₇Sn 3655.9
3223.6
3218.7
3330.6
Pb 3240.2
3119.2
N₈Pb 5005.5
N₉Pb 5005.5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

CALCIUM

Ca

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 035.0	4	I 3 973.7	6	3	I 5 270.3	10	10
2 040.0	4	I 4 098.6	4	2	5 349.5	10	5
I 2 275.5	1	4R	I 4 226.7†FB ₁	10R	10R	I 5 512.9	8	2
I 2 398.6	8R	1R	I 4 240.4	4	2	5 582.0	8	4
2 493.0	7	I 4 283.0	8R	8R	5 588.7	10	10
2 899.8	9	I 4 289.4	8R	8R	5 590.1	10	6
2 924.3	8	I 4 299.0	6	8R	I 5 594.5	8	6
I 3 000.9	4	2	I 4 302.5	10R	10R	5 598.5	10	8
I 3 006.9	4	4	I 4 307.7	8R	8R	I 5 601.3	8	4
3 119.7	8	I 4 318.7	8R	8R	5 602.8	8	5
II 3 158.9L	8	10R	I 4 355.2	6	2	5 857.5	10	10
II 3 179.3L	6	10R	I 4 425.4	10R	10R	5 867.6	4
II 3 181.3	4	10	I 4 435.0	10R	10R	I 6 102.7	8R	8R
I 3 225.8	4	I 4 435.7	8R	8	I 6 122.2	10R	10R
I 3 286.1	5	I 4 454.8p	10R	10R	I 6 161.3	5	2
I 3 344.5	5	I 4 455.9p	8R	8	I 6 162.2	10R	8R
I 3 350.2	6	1	I 4 456.6p	4	5	I 6 163.8	4	2
I 3 361.9	6	1	4 490.9	10	I 6 166.5	4	2
I 3 468.5	4	I 4 527.0	6	5	I 6 169.1	4	3
I 3 474.8	4	I 4 578.6	8	5	I 6 169.6	7	3
I 3 487.6	6	1	I 4 581.5	8	6	I 6 439.1	10R	8
I 3 624.1	6	1	I 4 585.8	6	6 449.8	5	3
I 3 630.7	6	1	I 4 585.9	2	8	I 6 402.6	6R	6
I 3 631.0	5	1	I 4 685.2	4	1	I 6 471.7	5	5
I 3 644.4	10	4	I 4 878.2	10	8	I 6 493.8	8	5
I 3 644.8	5	I 5 141.7	8	3	I 6 499.6	5	4
II 3 706.0	6	8	I 5 188.8	6	5	I 6 717.7	8	2
II 3 736.9	6	10R	I 5 260.4	4	3	7 148.2	10
II 3 938.7p*L	10R	10R	5 261.7	6	5	7 202.2	8
I 3 948.9	4	1	5 262.2	6	5	I 7 326.1	8
I 3 957.1	6	2	I 5 264.2	6	5	7 610.0	6
II 3 968.5ptL	10R	10R	5 265.6	8	8			

Control lines: Interfering lines:

*Co 3929.3 *Ba Co Fe Mn Mo Se

Fe 3899.7

†Cr 3963.7 †Al Co Cr Fe Mo Ni

Control lines: Interfering lines:

Fe 3930.3

†Co 4248.2

Fe 4236.0

‡Co Cr Fe Ge Mn Mo

CARBON

C

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
III 2 297.6	2	10	III 4 648.70	3	III 4 652.68	7
I 2 478.3P*	10	10	III 4 651.46	2			

Control lines: Interfering lines:

*Fe 2470.7

*Hg Sb

Control lines:

W 2481.5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
CERIUM

Ce

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 651.0	4	1	3 999.3	10	6	5 191.6	5	1
2 696.1	4	4 012.4P	10	10	5 211.9	4
2 791.4	4	4 040.8P	9	8	5 274.2	5	3
2 833.3	4	4 073.5	9	4	5 330.5	5	2
2 896.8	4	4 083.2	10	5	5 393.4	7	3
2 976.9	4	1	4 106.9	5R	3	5 409.2	6	3
3 017.2	4	1	4 133.8†	10	10	5 472.3	5	3
3 052.0	5	1	4 137.6§	9	10	5 512.1	8	3
3 063.00	6	2	4 149.9	10R	10	5 556.3	4	1
3 103.4	6	1	4 152.0	8	10	5 601.3	5	1
3 146.4	6	1	4 165.6P	9	10	5 655.1	5	1
3 171.6	6R	1	4 186.6P	10	10	5 670.0	5	1
3 194.8	7	1	4 222.6	10	5	5 677.7	4	1
3 201.7	7	1	4 248.7	8	6	5 697.0	5	1
3 221.2	7	1	4 255.8	8	3	5 699.2	5	1
3 234.2	7	1	4 289.9	9	6	5 719.0	5
3 272.3	7	2	4 296.7	9	8	5 725.8	4
3 285.2	6	1	4 306.7	8	4	5 743.5	5
3 304.8	7	1	4 320.7	8	3	5 768.9	4	1
3 344.8	7	2	4 337.8	9	4	5 773.1	4
3 366.6	7	1	4 349.8	8	4	5 788.2	4
3 377.1	7	2	4 375.2	8	3	5 804.4	4
3 426.2	8	1	4 382.2	8	5	5 812.9	5
3 442.4	7	1	4 391.7	8	8	5 838.1	4	1
3 476.8	6	2	4 418.8	7	5	5 862.5	4
3 485.1	8	2	4 449.3	9	4	5 910.0	5R
3 488.6	7	1	4 460.2	10	10	5 928.3	4
3 517.4	7	2	4 471.2	10	5	5 934.4	4
3 539.1	7	2	4 509.2	4R	3	5 940.9	4	1
3 560.8*	8	4	4 527.4	10	5	5 975.9	4
3 577.5	8	4	4 528.5	10	5	6 013.4	5
3 613.7	10R	2	4 539.7	10	5	6 024.2	5
3 623.8	7	3	4 562.4	10	10	6 043.4	5	2
3 655.9	10	3	4 572.3I.	10	10	6 098.4	4	1
3 668.0	9	3	4 593.9	10	10	6 123.7	4
3 679.4	6	2	4 606.4	4	5	6 229.0	4	1
3 709.3	8	3	4 628.2	10	10	6 272.1	4	2
3 716.4	9	3	4 654.3	4	2	6 344.0	4	1
3 764.1	8	3	4 684.6	4	3	6 371.1	4
3 786.0	8	3	4 714.0	4	3	6 393.1	3	1
3 801.5†	10	8	4 725.1	4	2	6 458.1	3
3 853.2	8	2	4 737.2	4	3	6 467.4	3
3 875.0	6R	2	4 773.9	4	3	6 513.6	3
3 878.4	9	2	4 882.4	4	3	6 606.9	3
3 890.0	8	3	4 971.5	4	2	6 652.8	3
3 942.8	10	5	5 022.9	4	1	6 700.7	3
3 952.6	9R	8	5 044.0	4	1	6 924.8	3
3 956.3	9	3	5 079.7	5	2	7 061.7	3
3 992.4	9	3	5 117.1	4	1	7 086.3	3
3 993.8	9	4	5 187.4	2	6	7 252.7	3

Control lines: Interfering lines:

*Co 3533.4

*Co Cr Fe Hg Os

†Fe 3795.0

†Co Cr Fe Hg Mn Sn Ti W

‡Fe 4123.8

‡Ba Co Cr Fe Li Mn Sb Se Ti

Control lines:

§Os 4260.9

||Fe 4187.1

Interfering lines:

§Co Fe Mn Mo Ni Pt

||Co Cr Fe Mn Mo Ni

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)

PRINCIPAL LINES BY ELEMENTS

CESIUM

Cs

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 035.7	8	3 268.3	10	I 4 593.0p†	10R	3.
2 080.6	8	3 300.0	8	II 4 603.8	10	10
2 089.2	8	3 316.0	8	4 616.1	4
2 102.4	10	3 340.5	8	4 623.1	4
2 132.4	10	3 349.4	8	II 4 646.5	5
2 142.2	10	3 411.3	9	4 763.6	5
2 147.5	10	3 559.8	5	II 4 830.2	0
2 180.2	9	3 597.4	6	4 870.0	0
2 206.3	10	3 608.3	5	II 4 952.8	6
2 221.3	10	3 661.4	6	II 4 972.6	5
2 268.3	10	3 699.5	5	II 5 043.8	0
2 274.5	10	II 3 785.4	5	II 5 096.6	4
2 495.0	8	II 3 805.1	6	II 5 227.0	8
2 526.0	10	II 3 897.0	7	II 5 249.4	6
2 544.0	10	II 3 925.6	6	5 274.0	4
2 573.1	8	II 3 965.2	6	II 5 371.0	6
2 596.9	10	3 974.2	6	5 402.8	4
2 600.4	8	4 006.5	6	II 5 419.7	5
2 630.6	10	4 039.8	9	II 5 563.0	4
2 700.0	8	4 068.0	6	II 5 831.2	5
2 707.0	10	II 4 068.8	6	5 925.7	5
2 776.0	10	4 158.6	4	6 010.4	4	2
2 811.0	6	4 213.3	6	II 6 128.6	4
2 838.0	8	4 232.2	6	6 213.0	8	2
2 845.0	10	4 264.7	10	6 354.5	4	1
2 859.4	10	II 4 277.1	9	6 562.8	5
2 887.0	10	II 4 288.4	7	I 6 586.5	10	1
2 894.0	8	4 300.6	6	I 6 587.1	5
2 931.1	10	II 4 373.0	6	I 6 723.3	10R	3
2 938.0	8	II 4 384.4	5	II 6 955.5	4
2 963.0	8	4 405.3	7	I 6 973.3	10R	3
2 976.9	6	II 4 435.7	4	I 6 983.4	6	1
3 066.7	10	4 501.5	7	I 7 228.6	5	1
3 149.6	8	II 4 526.7	7	I 7 280.0	5	1
3 152.7	6	II 4 538.9	6	I 7 609.0	8
3 211.0	6	I 4 555.5p*F	10R	4			

Control lines: Interfering lines:

*Be 4535.5 *Al Ba Be Co Cr Cu Fe

Ti 4552.5 Mo Ni Pb Pt Si Ti

Ti 4522.8

Control lines: Interfering lines

†Al 4576 †Al Ba Be Co Cr Fe Li

V 4395.2 Mo Ni Pd Sb Se

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

CHROMIUM

Cr

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 324.9	4	II 3 132.1	4	10	I 4 337.6	6R	9
2 538.3	5	3 180.7	3	10	I 4 339.5	6R	5
2 591.9	4R	1	3 197.1	3	10	I 4 339.7	5R	4
2 677.2	5R	10	3 209.2	2	10	I 4 344.5	7R	8
2 678.8	4	10	3 217.4	3	8	I 4 351.1	5R	4
2 691.1	4	10	3 307.1	1	8	I 4 351.8	7R	9
2 731.9	5R	1	II 3 339.8	3	10	I 4 359.6	6R	8
II 2 743.6	3	8	II 3 342.6	3	10	I 4 371.3	6R	9
II 2 750.7	3	10	3 346.7	4R	1	I 4 385.0	6R	7
II 2 751.9	3	10	3 358.5	3	10	4 458.5	4	3
2 757.1	4R	2	3 360.3	3	10	4 465.4	4	4
II 2 762.6	3	10	3 368.1	4	10	I 4 496.9	6R	10
II 2 766.5	4R	10	3 382.7	2	10	4 511.9	4	6
2 769.9	6R	1	3 403.3	2	10	4 540.7	4	6
2 780.7	7R	3 408.8	3	10	I 4 546.0	5R	6
2 792.2	1	10	3 421.2	3	9	I 4 580.1	7	3
2 800.8	1	10	3 422.7	3	10	I 4 591.4	6	2
2 812.0	2	10	3 433.6	5R	2	I 4 600.8	6R	4
2 822.4	2	10	3 550.6	4	2	I 4 610.1	6R	6
2 830.5	2	10	I 3 578.7*LB ₁	10R	10R	I 4 626.2	6R	5
II 2 835.6P	5R	10	I 3 593.5†	10R	10R	I 4 646.2	7R	10
II 2 843.3P	4	10R	I 3 605.3‡L	10R	10	I 4 652.2	6R	5
II 2 849.8P	4	10	3 636.6	5R	3	4 708.0	7	3
II 2 855.7P	4	10	3 639.8	6R	5	4 718.5	7	6
II 2 862.6	3	10	3 743.6	4R	3	4 737.3	5	3
2 910.9	4R	1	3 743.9	4R	3	4 756.1	6	8
2 967.6	4R	1	3 749.0	4R	3	4 789.4	5	3
2 971.9	2	10	3 804.8	5	3	4 801.0	5	2
2 979.7	2	10	I 3 885.2	5R	3	4 829.4	5	4
2 985.3	2	10	I 3 894.1	4R	3	4 922.3	4	3
2 986.5	6R	2	I 3 908.8	6R	3	4 954.8	4	2
2 989.2	2	10	I 3 919.2	7R	5	5 166.2	3	4
2 995.1	4R	1	I 3 921.0	5R	3	I 5 204.5p	9R	10
2 996.6	4R	1	I 3 928.7	6R	3	I 5 206.0p	10R	10
2 998.8	4R	1	I 3 941.5	5R	3	I 5 208.4	10R	10
3 005.1	5R	1	3 963.7	7R	8	I 5 247.6	5R	3
3 014.8	5R	1	3 969.8	7R	8	I 5 264.2	6R	5
3 014.9	6R	1	3 976.7	7R	8	I 5 265.7	5R	3
3 017.6	6R	2	3 983.9	7R	5	I 5 275.2	4	5
3 018.5	5R	1	3 991.1	6R	4	I 5 296.7	5	6
3 021.6	6R	2	4 001.5	4	2	I 5 298.3	6	10
3 034.2	5R	1	4 026.5	4	2	I 5 328.4	10	8
3 037.1	5R	1	4 058.8	4	3	I 5 345.8	10	6
3 040.9	5R	10	4 109.6	4	1	I 5 348.3	10	5
3 050.1	2	10	4 163.6	4	4	I 5 409.8	10	8
3 053.9	6R	2	4 179.3	4	3	5 664.0	4	2
II 3 118.7	3	10	I 4 254.3P‡LB ₂	10R	10R	5 694.7	5	2
II 3 120.4	4	10	I 4 274.8p‡LB ₃	10R	10	5 698.3	5	2
II 3 125.0	4	10	I 4 289.7p‡LB ₁	10R	10	5 712.8	4	2

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 CHROMIUM (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
5 781.8	7	1	I 6 362.9	5	3	I 6 925.2	9
5 783.1	8	3	6 661.1	5	2	6 978.5	10
5 783.9	9	3	6 669.3	4	I 6 979.8	7
5 785.0	8	3	I 6 881.7	9	I 7 356.0	10
5 788.0	9	6	I 6 882.4	9	I 7 400.3	10
5 791.0	10	8	6 883.0	9	I 7 462.4	10
I 6 330.1	6	3	I 6 924.2	10			

Control lines:	Interfering lines:	Control lines	Interfering lines
*Co 3569.4	*Ba Co Hg Mn Mo	Fe 4307.9	
Fe 3719.9		Ti 4337.9	
Mo 3624.5		¶Ca 4283.1	¶Ba Be Ca Co Cs Fe
†Co 3518.4	†Ba Bi Cu Sb	Mo 4232.6	Ni Pb Pt Ti V
Ni 3610.5		Ti 4298.7	
‡Co 3594.9	‡Co Fe Mn V	B ₁ Ni 3619.4	
Fe 3618.8		B ₂ Fe 4245	
§Fe 4260.5	§Be Bi Co Cu Fe Mo	B ₃ Fe 4247	
Cu 4651.2	Co Cu Fe Li Mo Pt	B ₄ Fe 4352	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

COBALT

Co

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 011.5	7	3 346.9	10	2	I 3 842.1	6R	10
2 105.0	4	1	I 3 354.4	6R	4	I 3 845.5	10R	10
2 196.6	5	3 377.1	8R	1	I 3 861.2	7R	10
2 286.2P	2	6R	I 3 385.2	9R	4	I 3 873.1	9R	10
2 307.9p	2	6R	I 3 388.2	9R	5	I 3 876.8	8R	5
2 363.8	2	10	I 3 395.4	10R	5	I 3 894.1	9R	10
2 378.0p	2	10	I 3 405.1*	7R	10	I 3 936.0	6R	10
2 388.9pF	2	10R	I 3 409.2	4R	6	I 3 941.7	5R	4
2 397.4	1	10	I 3 412.3†	4R	4	I 3 957.9	6R	4
2 432.3	3R	5	I 3 433.0	6R	6	I 3 974.7	5R	4
2 447.7	10	I 3 443.7	3R	6	I 3 995.3‡	8R	10
2 464.2	2	8	I 3 449.2	6R	5	I 3 997.9	7R	10
2 506.4	3	10	I 3 449.5	6R	5	I 4 020.9	7R	5
2 511.1	2R	4	I 3 453.5P†LB ₁	6R	10	I 4 045.4	8R	5
2 519.8	1	10	I 3 462.8	6R	5	I 4 066.4	7R	5
2 529.0L	3R	2	I 3 465.8p	6R	5	I 4 086.3	8	9
2 542.0	2	10	I 3 474.0	9R	8	I 4 092.4	8R	8
2 559.4	3	10	3 485.4	7	3	I 4 110.5	9	10
2 564.0	3	10	I 3 489.4	5R	7	I 4 118.8†	8R	10
2 580.3L	4	10	I 3 495.7	6R	5	I 4 121.3**	10R	10R
2 632.4	10	I 3 502.3§	5R	6	4 160.7	1	8
2 648.7	4	10	I 3 506.3	6R	8	I 4 190.7	7	4
2 663.5	4	10	I 3 509.9	4R	5	4 252.3	5	2
2 676.0	4	4	I 3 510.4	4R	4	4 339.6	5	3
2 731.1	4	2	I 3 512.6	4R	6	I 4 469.6	8	5
2 745.1	4	3	I 3 513.5	4R	4	4 531.0	7	10
2 766.2	4	2	I 3 518.4	6R	7	4 549.7	6	5
2 815.6	4	1	I 3 520.1	4R	3	4 565.6	7	7
2 886.6	5	2	3 521.6	5R	5	I 4 581.6	8	8
I 2 987.2	5R	3	I 3 523.4	4R	5	4 594.6	6	3
I 2 989.6	6R	3	I 3 526.9	9R	6	4 596.9	6	3
I 3 044.0	8R	4	I 3 529.0	4R	3	I 4 629.4	8	4
I 3 072.3	5R	3	I 3 529.8p	8R	6	I 4 663.4	8	4
I 3 082.6	5R	3	I 3 533.4	6R	4	I 4 682.4	7	3
I 3 086.8	6R	3	I 3 550.6	5R	3	I 4 749.7	8	3
I 3 137.3	6R	3	I 3 565.0	5R	4	I 4 792.9	7	7
I 3 139.9	7R	3	I 3 569.4	7R	10	I 4 813.5	8	10
I 3 147.1	7R	3	I 3 575.0	5R	4	I 4 840.3	8	8
I 3 149.3	6R	2	I 3 575.4	6R	5	I 4 867.9	8	8
I 3 158.8	6R	3	I 3 587.2	8R	10	I 4 972.0	6
I 3 159.7	6R	1	I 3 602.1	5R	4	I 5 122.8	5	1
3 243.8	8R	2	I 3 627.8	8R	4	5 133.5	5	1
3 247.2	7R	2	3 639.4	10	2	5 176.1	6
3 254.2	10R	2	3 676.6	8	6	I 5 212.7	5	1
3 260.8	7R	2	3 683.1	8	8	I 5 230.2	5	1
3 265.4	6R	1	I 3 704.1	8	7	5 266.5	6	1
3 283.5	10R	3	3 732.4	8	7	I 5 280.6	5	1
3 319.5	10	2	I 3 745.5	6R	10	5 342.7	8	2
I 3 334.2	5R	4	3 755.5	6R	4	5 343.4	7	2

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 COBALT (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 5 352.1	8	2	6 211.1	8	1	I 7 052.9	10
5 353.5	7	2	6 231.0	7	3	7 054.04	8
5 362.8	8	1	6 257.6	10	3	I 7 085.0	10
I 5 369.6	7	1	6 271.4	10	7 134.3	8
5 444.6	8	1	I 6 282.7	10	4	I 7 154.7	8
5 454.6	9	1	6 320.4	10	2	7 159.2	8
I 5 483.4	10	2	6 347.8	10	1	7 193.6	8
I 5 530.8	8	1	6 395.2	7	1	7 285.3	7
I 5 590.7	8	1	6 417.8	8	1	I 7 354.6	6
5 647.2	8	1	6 429.9	7	7 388.7	7
5 830.1	7	I 6 450.2	10	6	I 7 417.4	8
5 890.5	7	2	6 455.0	10	5	7 457.4	8
5 915.5	8	3	6 477.9	9	7 554.0	8
5 946.5	8	1	6 490.3	7	1	7 590.6	6
I 5 984.2	10	2	6 563.4	9	3	7 610.3	6
5 991.9	10	5	6 595.9	6	3	7 712.7	9
6 000.7	8	1	6 617.3	10	1	7 734.3	6
6 006.3	8	2	6 632.4	6	2	7 838.2	8
6 007.6	8	2	I 6 678.8	6	7 840.1	7
6 049.1	10	2	I 6 771.1	10	2	7 855.9	7
6 082.5	10	5	I 6 815.0	10	1	7 869.9	6
6 086.7	7	2	6 872.4	7	2	7 871.4	6
I 6 093.1	6	2	6 937.8	7	7 908.8	10
6 107.9	7	1	I 7 016.6	10	7 926.6	8
6 122.7	10	2	7 027.8	8	7 987.4	7
I 6 188.9	8	3						

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Cd 3466.2	*Bi Cd Cr Cu Mo	\$Ba 4166.0	\$Ag Ba Cr Mo Ni
Cr 3368.1		Fe 3558.5	
Fe 3521.3		Ti 3394.6	
†Cr 3368.1	†Bi Cr Cu Fe Mn	Ba 4166.0	Ba Cr Fe Mn Mo
Ni 3524.5		¶Fe 4181.8	¶As Cr Ge Mn Mo
‡B 2496.8	‡Cr Mo Ni Pb Pt	**Fe 4120.2	**As Bi Cr Cu Fe Mn
Ni 3493.0		Bi 4722.2	Ni Ti V W
Ni 3472.6		Mo 4081.5	
		BiMn 3442.0	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS

COLUMBIUM

Cb

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 584.0	2	6	3 966.2	10	3	4 672.1	10	9
II 2 697.1	3	7	4 032.6	10	3	4 675.4	10	8
II 2 927.8B ₁	8	10	4 059.0P*	10	10	4 708.3	7	4
II 2 941.6	4	8	4 079.7p**	10	6	4 713.5	5	3
II 2 950.9	6	10	4 101.0††	10	6	4 733.9	5	3
II 3 094.2P*	10	10	4 123.0p	10	4	4 810.6	6	3
II 3 130.8p†	8	10	4 130.0	10	3	4 816.3	7	1
II 3 163.4p†	5	10	4 137.1p	10	4	4 924.8	3	8
II 3 195.0p§	5	10	4 139.7	10	4	4 989.0	5	2
II 3 225.5p	5	10	4 152.6	10	5	5 039.0	6	2
II 3 236.4	3	10	4 163.6	10	10	5 079.0	8	3
3 342.0	10	4	4 164.7	10	5	5 095.3	10	3
3 358.4	10		4 168.1	10	5	5 134.7	5	2
3 498.6	10	2	4 190.9	10	4	5 160.3	6	3
I 3 510.3	3	8	4 192.1	10	3	5 164.4	7	2
I 3 535.3	10	3	4 205.3	10	3	5 180.3	6	2
I 3 537.5	10	2	4 214.7	10	3	5 271.5	9	3
I 3 554.6	10	2	4 218.0	10	3	5 276.2	10	3
I 3 563.5	10	2	4 229.2	10	3	5 344.2	10	5
I 3 575.9	10	2	4 262.1	8	3	5 350.7	7	3
I 3 580.3	10	3	4 299.6	8	4	5 437.3	7	2
3 697.8	10	3	4 301.1	10	5	5 551.4	6	2
3 713.1	10	3	4 326.4	10	3	5 664.7	6	2
3 726.2	10	3	4 331.4	10	3	5 665.6	6	3
3 739.8	10	3	4 351.6	10	3	5 671.1	7	1
3 740.8	10	5	4 377.9	10	4	5 729.2	6	2
3 742.4	10	3	4 410.2	10	3	5 787.5	6	2
3 759.6	10	3	4 437.2	10	8	5 819.5	6	3
3 787.1	10	3	4 447.2	10	3	5 838.7	8	5
3 790.1	10	3	4 523.4	8	3	5 866.5	6	3
3 791.2	10	4	4 546.8	10	4	5 900.6	10	2
3 798.1	10	4	4 573.1	10	5	5 983.3	7	2
3 803.0	10	4	4 581.6	10	5	6 430.5	8	1
3 810.5	10	3	4 606.8	10	10	6 544.7	6	1
3 818.9	1	8	4 630.1	10	10	6 677.3	8	1
3 914.7	10	3	4 648.9	7	3	6 723.7	6	1
3 937.5	10	3	4 663.8	9	4	6 828.1	4	..

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Al 3961.5

*Al Bi Cr Cu Mg V

Mo 3170.3

Au Ba Co Cr Fe

Fe 3222.1

Fe 3719.9

Mg 2779.9

Mo 3624.5

†Be 2348.6

†Cr Mn Ti V W

*Fe 4059.7

*Co Cr Fe Mg Mn

Cr 2849.8

Mn 4048.8

Pt Ti W

Hg 3650.2

**Mn 4051.6

**Ba Bi Co Cr Cu Fe Mg

Mo 3864.1

Mo 4069.9

Mo Ni Pt Se Sr Ti V

Ni 3012.0

Se 4020.4

†Ti 3168.5

†Cr Mn Mo V W

Ti 4295.8

Ti 3162.6

††V 4095.3

††Cr Fe Mn Mo Ni In Ti

§Cr 3180.7

§Au Cr Cu Mn Mo

V 4105.0

Fe 3222.1

B₁Mn 2933.1

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
COPPER

Cu

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
+ 2 112.105	2	3	2 997.4	6	4	I 3 457.9	4	1
+ 2 126.047	2	3	3 010.9	7	1	3 483.8	6	3
2 149	1	3	3 036.1	8	2	I 3 512.1	6	3
+ 2 189.631	2	4	I 3 063.4	7	3	3 520.0	4	1
2 192.3S ₂ N ₃	3	4	3 073.8	5	2	3 527.5	5	1
2 199.6	4R	2	3 094.0	6	2	3 530.4	7	2
I 2 214.6	4R	2	3 099.9	6	3	3 533.7	7	1
+ 2 218.07	1R	5	3 108.6	8	5	I 3 599.1	8	2
I 2 227.8	4R	2	3 116.3	7	2	3 602.0	8	2
2 230.1	4R	2	3 126.1	7	3	3 621.2	6	2
+ 2 242.22	2	6	3 128.7	6	2	3 654.6	6	3
2 247.0	3	6R	3 140.3	6	2	3 683.6	6	3
I 2 263.1	3R	2	3 142.4	7	2	3 700.5	3	1
2 276.261	1	4	3 146.8	6	2	3 741.3	3	1
2 293.9	6R	3	I 3 194.1	8	3	3 771.9	3	1
2 294.3	3	5	3 208.2	6	2	I 3 861.8	3	1
+ 2 303.134	4	3	3 231.2	4	2	I 4 022.7	10	8
2 356.6	2	4	3 243.2	6	4	I 4 062.7	10	7
I+ 2 369.891L	5	8	I 3 247.6*FL	10R	10R	I 4 063.4	6	1
I 2 392.6	7	1	S ₂ B ₂ N ₁			4 177.7	6	2
2 400.1	2	5	I 3 274.0p†	10R	10R	4 249.0	6	4
I 2 441.6	5	2	LS ₂ B ₂ N ₂			4 275.1	8	8
2 473.5	1	4	3 279.8	5	3	4 378.2	8	8
I 2 492.2	5R	2	3 290.6	10	6	I 4 480.4	7	2
2 506.4	1	6	3 293.9	4R	2R	4 509.4	6	3R
2 529.4	1	5	3 308.0	9	7	I 4 530.8	8	2
I 2 618.4	10R	3	3 317.2	5	2	4 587.0	10	10
2 701.1	1	5	3 337.9	8	3	4 651.2	8	7
2 713.6	1	5	3 365.4	6	2	4 674.8	5	3
I 2 766.4	10	4	3 381.4	3	1	4 704.6	4	2
2 824.4B ₁	10	5	3 402.2	4	1	5 016.6	2	2
2 883.0	6	3	3 450.3	7	6	I 5 105.6	7	6
2 961.2S ₂ B ₂	9	6	3 454.7	6	3			

Control lines: Interfering lines:
 *Ti 3252.9 *Co Cr Fe Mo
 †V 3271.1 †Ca Mo Se
 V 3267.7

Control lines:

S₁Pb 2189.7
 S₂Pb 2980.3
 S₃Pb 3220.5
 3240.2
 S₁Pb 3240.2
 3220.5
 2657.2
 B₁Sn 2850.6
 Zn 3075.9
 B₂Sn 3032.8
 3009.1

Control lines:

B₂Fe 3246.0
 Pb 2833.1
 Mg 2802.7
 B₂Fe 3271.0
 Sn 3262.3
 N₁Sn 3223.6
 3218.7
 3141.8
 Pb 3262.4
 3240.2
 3220.5

Control lines:

3119.2
 N₂Sn 3262.3
 3223.6
 3218.7
 3141.8
 Pb 3262.4
 3240.2
 3220.5
 3119.5
 N₃Sn 2282.2
 Pb 2190.0

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

DYSPROSIUM

Dy

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
3 407.8L	8	3	3 968.4	10	10	4 589.4	10	5
3 408.1L	8	3	3 978.6	6	10	4 612.3	8	4
3 454.4	6	10	4 000.5p	8	10	4 731.8	10	3
3 494.5	8	5	4 046.0p	10	4	4 957.4	10	2
3 524.0	5	10	4 078.0pL	10	10	5 139.6	8	1
3 531.7L	10	10	4 103.3	8	8	5 197.7	8
3 550.2	8	10	4 111.4	8	4	5 380.7	6
3 600.3	6	10	4 168.0p	10	4	5 389.6	6
3 645.4L	8	10	4 186.8	8	4	5 652.0	6
3 676.6	3	10	4 194.9	8	4	6 088.3	6
3 694.8	6	10	4 211.7p	10	5	6 168.5	6
3 698.2	4	10	4 221.1	8	3	6 259.1	10
3 806.3	6	10	4 256.3	8	3	6 422.0	6
3 898.5	6	10	4 409.4	8	3	6 579.4	6
3 944.7L	10	10	4 449.7	8	8	6 667.9	6

ERBIUM

Er

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
3 372.8L	10	10	4 194.8	10r	2	5 255.9	6	2
3 499.1p	10	10	4 375.0	10	6	5 395.9	6	2
3 599.8	5	8	4 419.6	8	10	5 414.6	6	1
3 692.7p	10	4 500.8	8	6	5 826.8	6	1
3 766.3	10	3	4 675.6	5	10	6 221.0	6	1
3 906.3p	10	10	4 795.5	8	3	6 308.8	8
3 938.7	8	4	4 831.1	8	3	6 388.2	6
4 008.0	10	4	4 951.7	8	3	6 601.1	6
4 087.7	10	1						

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

EUROPIUM

Eu

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
3 688.4	10	10	4 661.9	10	10	6 173.0	10	3
3 725.0	10	10	4 911.4	8	2	6 188.1	10	2
3 819.6L	10R	10	5 357.6	9	1	6 262.3	10	2
3 907.1	10	10	5 402.8	10	2	6 303.4	10	3
3 930.5L	10	10	5 451.5	9	2	6 350.0	10	1
3 972.0L	10	10	5 453.0	9	2	6 437.6	10	5
4 129.7	10	10	5 547.4	10	1	6 645.2	10	10
4 202.0	10	5 570.3	10	1	6 802.8	10
4 205.0p	10	10	5 577.1	9	1	6 864.6	10
4 435.5	10	10	5 832.0	10	3	7 077.1	8
4 522.6	10	10	5 967.1	10	1	7 194.8	8
4 594.1	10	10	6 083.9	9	1	7 217.6	8
4 627.3	10	10						

GADOLINIUM

Gd

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 628.1L	10	3 656.2	7	8	4 251.8	8	10
2 655.6L	6	3 684.6	7	10	4 262.1	9	10
2 679.4L	8	3 671.2	10	8	4 297.1L	4	4
2 717.3L	8	3 712.7	6	10	4 325.7	9	5
2 904.7L	10	3 719.5	9	10	4 327.1	8	4
2 955.5	10	3 743.4	7	10	4 342.2L	10	10
3 032.9L	7	8	3 768.4p	10	10	4 346.5	8	2
3 034.1L	7	6	3 796.4	9	10	4 406.7	4	10
3 082.0	10	6	3 814.0	9	6	4 419	5	8
3 100.5	8	8	3 852.5	10	8	4 421.3	3	8
3 350.5	7	10	3 916.6	9	8	4 436.2	6	10
3 358.6	7	8	4 037.3	9	6	4 438.2	5	8
3 362.3	6	10	4 049.9	8	6	4 540.0	4	10
3 422.5	8	10	4 063.5	10	5	4 614.5F	4	2
3 481.3	6	8	4 070.4	9	5	4 639.0F	4	3
3 545.8	9	10	4 073.8	8	8	5 393.6	8
3 549.4	7	10	4 085.6	8	8	5 696.2F	8
3 585.0	8	10	4 098.6	8	6	6 846.6	8
3 592.7	5	8	4 130.4	10	10	6 996.8	10
3 646.2p	10	10	4 137.1L	6	8	7 168.3	10
3 654.6	7	8	4 184.3	9	10			

For explanation of control and interfering line symbols see page 1

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

GALLIUM

Ga

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 719.7	3	8	I 2 943.7†L	10R	2	4 172.1P§F	10R	10R
2 780.2	9	2 944.2L	5R	1	I 6 396.8	10	5
I 2 874.2*L	10R	2	4 033.0p†FL	10R	10R	I 6 413.7	SR

Control lines: Interfering lines:

*Cr 2865.1 *Ag Cu Fe Pb Ti V
Fe 2941.3
Mo 2848.2
Pb 2814.2
Sb 2698.1

Control lines:

†Fe 2912.2
V 2808.8
‡Mn 4030.8
V 4005.7
§Os 4112.0

Interfering lines:

†Bi Cs Cr Fe Mg Mn
‡Co Cr Fe Mo Sb Sr Ti
§Au Co Cr Fe Mo Mn

GERMANIUM

Ge

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 417.3	3	10	I 2 754.6§	10	10R	I 4 226.7p	7	10
I 2 502.6*	10	10R	I 3 039.1p L	10R	10R	4 260.8	10
I 2 651.2p†	10	10R	3 067.0	7	1	I 4 685.8	5	10
I 2 651.6p	10	10R	I 3 124.8	10	5	4 814.7	9
I 2 691.4	10	10	I 3 269.5p	10	10	5 131.7	7
2 709.7‡	10	10R	4 179.0	10	5 229.37	6
2 740.44	8	7						

Control lines: Interfering lines:

*Fe 2588.0 *Cd Co Fe Mn Mo Sn
Mn 2576.1
†Al 2660.3 †Al Be Hg Mg Mn Mo
Be 2348.6
Cr 2663.4

Control lines:

‡Mn 2705.7
V 2739.7
§Cr 2750.7
Fe 2749.3
||Cr 3053.9
Fe 3047.6

Interfering lines:

‡Mn Mo Ti W
§Co Fe Pt
||Fe Hg Mo Pt W

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

GOLD

Au

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 000.6	3	I 2 748.3S ₁	6R	4	3 586.7	5
2 082.0	3	2 780.8	3	3 633.3	3
2 201.3	3	2 802.2	10	3 649.1	3
2 229.0	3	2 820.0	8	3 706.8	4
2 242.7	3	2 822.7	3	3 804.0	5
2 283.3	3	2 825.4	4	3 825.7	3
2 291.5	3	2 838.0	3	I 3 897.9	4	8
2 304.8	4	I 2 883.5	4	3	4 016.1	4
2 314.7	3	I 2 892.0	4	2	4 052.8	5
2 340.2	3	2 905.9	6	3	I 4 065.1	6	8
I 2 352.7S ₁	4	3	2 907.1	4	I 4 241.8	1	3
I 2 364.6	4	2	2 913.5	4	10	I 4 315.1	1	3
I 2 376.3	3	2	2 932.2	5	4	I 4 437.3	4	3
I 2 387.8	4	3	2 954.4	4	I 4 488.3	4	4
I 2 428.0P*LS ₂	10R	10R	2 990.3	5	I 4 607.4	4	2
2 503.3	5	2 995.0	5	I 4 792.6	8	6
I 2 510.5	4	2	I 3 029.2	6	5	I 4 811.6	3	2
I 2 544.2	4	2	3 117.0	4	1	5 230.3	2	3
I 2 590.1	4	2	3 122.5	5	5 759.9	3
I 2 641.5	4	4	I 3 122.8S ₆	6R	8	I 5 837.4	4	6
I 2 676.0p†FLS ₂	10R	10	I 3 194.7	4	2	I 5 863.0	2	3
2 687.6	3	I 3 204.7	4	3	I 5 957.0	2	3
2 688.2	3	3 230.6	3	3	I 6 278.2	4	3
I 2 688.7	4	3	I 3 320.2	3	2	I 7 510.7	5
I 2 700.9	4	3	3 553.6	2	4			

Control lines:	Interfering lines:	Control lines:
*Sn 2706.5	*Ag Mn Pb Pt Sb Sn Sr	Pt 2650.9
W 2431.0		Ta 2685.1
W 2435.9		V 2677.8
†Cr 2835.6	†Co Cu Fe Sb V W	V 2679.4

Control lines:	Control lines:	Control lines:
SiPb 2253.9	SiPb 3240.2	SiPb 2657.2
SiPb 2411.8	3262.4	SiPb 3240.2
2428.8	2657.2	3119.1
	2926.8	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

INDIUM

In

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 062.7	8	I 2 713.9	6R	1	I 4 511.3P§L	10R	10
2 079.2	4	10	I 2 753.9	6R	3	4 638.9	10
I 2 306.1	5	7	2 836.9	8	4 656.6	10
I 2 340.2	6R	I 2 932.7	6R	4	4 681.9	10
I 2 389.6	8R	2 941.2	8	5 248.6	10
I 2 460.1	6R	3 008.2	10	5 644.9	10
I 2 468.0	4R	I 3 039.4*F	10R	4R	5 819.9	4	10
I 2 521.4	8R	1	I 3 250.1†FL	10R	8R	I 6 847.8	8
I 2 560.2	8R	3	I 3 258.5L	6R	3	6 891.3	10
I 2 710.3	10R	3	I 4 101.8p†F	8R	10	6 900.4	6

Control lines: Interfering lines:

*Cr 3053.9 *Co Fe Ge Sb W

Fe 3047.6

Ni 3057.6

Pt 2830.3

†Cd 2288.0

†Bi Fe Mn Mo Pt

Control lines: Interfering lines:

Ti 3252.9

†Cb 4079.7

V 4095.5

§Ti 4522.8

†Cr Fe Mn Mo Ni

§Al Ce Ca Cr Cu Mg

Pb Pt Ti V W

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

IRIDIUM

Ir

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 372.8L	4	2	3 516.0	6	3	5 046.1	8
2 544.0*	5	4	3 522.1	6	4	5 123.7	8
2 639.7†	4	3	3 573.7	6	6	5 177.9	8
2 662.0	6	3	3 605.8	2	10	5 238.9	10
2 664.8‡	5	3	3 609.8	6	3	5 273.8	6
2 694.2§S ₁ G ₁	6	3	3 617.2	6	4	5 340.7	8
2 824.4	6	4	3 628.7	7	5	5 364.3	10
2 833.2	4	10	3 636.2	6	3	5 385.6	7
2 836.4S ₂ G ₂	4	2	3 675.0	4	4	5 391.0	7
2 839.2S ₄	6	2	3 731.4	4	8	5 449.5	10	1
2 840.2S ₃ G ₃	4	3	3 747.2	5	6	5 454.5	10
2 849.7p¶	7	4	3 800.1	6	6	5 620.1	6
2 924.8**LS ₃ G ₄	8	4	3 976.3	5	10	5 625.6	10
2 934.6S ₅ G ₅	6	3	3 992.1	6	6	5 709.3	6
2 936.7S ₇ G ₆	5	3	4 020.1	5	8	5 736.2	5
2 943.2	7	4	4 069.9	4	8	5 828.5	7
3 100.4	8	3	4 399.5	6	8	5 882.3	9
3 133.3††LS ₅ G ₇	6	5	4 426.3	6	4	5 894.1	10
3 220.8P††LS ₅ G ₈	8	5	4 616.4	6	2	6 067.9	7
3 266.5	8	3	4 938.1	10	6 110.7	8
3 368.5	8	3	4 070.5	8	6 288.3	7
3 437.1p	8	4	4 999.7	10	6 334.5	6
3 449.0	7	4	5 002.7	10	6 686.1	7
3 518.7p§§	9	8	5 015.0	10			

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Co 2535.9

*Au Fe Co Cs Mn Na

Fe 2844.0

Co 2564.0

Mg 2802.7

†Au 3029.2

†Al Cd Cr Fe Mn Mo

**Mo 2891.0

**Co Cu Hg Mn Mo Tl

Mn 2638.2

††Be 2348.6

††Au Be Cl Cr Hg Mo Se

‡Co 2587.2

‡Au Fe Mo Pb Pt

Cr 2849.8

Cr 2762.6

Hg 3650.2

Pb 2873.3

Ni 3012.0

§Fe 2704.0

§Au Fe Mn W

††Fe 3225.8

††Mn Mo Pb

||Cr 2860.9

||Ag Co Cu Cr Fe Mn

Ti 3242.0

Cu 2961.2

§§Co 3409.2

§§Ag Ce Co Cu Fe Mo Ni

Fe 2844.0

Fe 3521.3

¶Cr 2843.3

¶Cr Fe Ni Pd Sb Sn W

Ni 3619.4

Control lines:

Control lines:

Control lines:

S₁Pt 2698.4S₅Pt 3301.9G₅Pt 2919.3S₂Pt 2834.7

3204.1

2921.4

S₃Pt 2834.7

3200.7

G₂Pt 2919.3S₄Pt 2834.7

3156.6

2921.4

S₅Pt 2919.3

3230.3

G₁Pt 3156.6

2921.4

3212.5

G₃Pt 3301.9S₆Pt 2919.3G₁Pt 2698.4

3204.1

2921.4

G₂Pt 2834.7

3200.7

S₇Pt 2919.3G₁Pt 2834.7

3230.3

2921.4

G₃Pt 2919.3

3233.4

S₈Pt 3156.6

2921.4

3212.5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS

IRON

Fe

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 000.3	3	2 300.1	5	2 472.35	5
2 020.6	3	2 310.01	5	I 2 472.87	5
2 040.6	3	2 313.1	5	I 2 472.91	4	1
2 063.7	3	2 327.39	6	2 473.16	4
2 084.2	4	2 332.80	6	2 474.82	5	2
2 093.7	4	2 338.01	6	I 2 479.78	4	1
2 106.4	4	2 343.50	7	2 483.28 ⁺	5R	1
2 139.7	5	2 344.3	4	2 483.54	4
2 144.4	5	2 348.12	5	I 2 484.19	6
2 151.7	5	2 348.3	5	2 486.38	4	3
2 159.9	5	2 351.2	4	2 486.69	4	1
2 165.8	5	2 354.9	6	2 487.07	4	1
2 166.8	6	2 359.11	6	2 487.87	4	1
2 171.3	5	II 2 360.3	5	I 2 488.15	4	2
2 178.1	5	2 362.1	8	I 2 489.76	6
2 191.8	5	2 364.83	8	I 2 490.66	4
2 196.0	5	2 366.69	5	I 2 491.16	4
2 199.5	5	II 2 368.59	7	2 493.3	8
2 200.7	5	2 370.5	6	2 496.54S ₁	5	1
2 213.6	4	2 373.62	4	2 498.88S ₂	10
2 221.3	4	II+2 373.737	6	4	2 501.14S ₂	3
2 229.1	6	II 2 375.19	4	2 502.54S ₂
2 231.2 ⁺	7	2 379.28	4	3	2 507.90	4	1
2 240.6	5	2 380.76	4	3	I 2 510.84S ₂	6	1
2 245.6	6	II 2 382.04P*LB ₁	8	10	2 511.8	5
2 248.9	6	N ₁ S ₁	2 512.37	4
2 249.2	7	2 383.25	4	2	2 517.66	4	1
2 251.0	6	2 388.63	6	3	I 2 518.11S ₂	6	1
2 253.2	6	2 389.98	4	I 2 522.36S ₁₀	4	3
2 255.8	7	2 395.42	4	3	2 523.66S ₁₁	4	1
2 260.8	6	II 2 395.63p†S ₂	8	4	I 2 524.29	6	1
2 265.2	5	2 399.24	6	5	2 525.4	4
2 266.9	5	2 404.43	4	2	I 2 527.44	4	2
2 267.1	5	II 2 404.89pS ₂	6	6	I 2 529.14	6	1
2 267.6	5	2 406.66	6	4	I 2 529.84	6
2 272.8	5	II 2 410.53p	6	5	2 533.7	5
2 274.1	5	2 411.07	6	3	I 2 535.61	6
I 2 276.0	5	+2 413.310p	6	3	2 537.18	6
2 279.9	6	2 439.75	4	1	I 2 540.98	6
2 280.2	6	2 442.57	4	1	2 542.11	5	1
2 287.3	5	2 443.87	4	1	2 543.93	5	1
2 287.6	5	2 444.5	4	2 544.72	4
2 289.0	6	I 2 447.72	4	2	I 2 549.62	6
2 290.6	5	2 453.48	4	1	II+2 562.541	5	5
2 291.1	6	2 457.60	6	1	2 563.48	5	4
2 292.5	5	I 2 462.19	6	1	2 566.02	4	3
I 2 297.8	6	I 2 462.65	6	1	2 570.54	3	1
I 2 298.2	7	2 465.16	5	2 570.86	3	3
I 2 299.2	5	2 468.88	5	1	2 574.37	3	4

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 IRON (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 575.76	4	1	2 704.00	3	4	I 2 767.52	7	5
2 576.70	4	2 706.59	5	2	2 772.08	4
2 576.87	4	3	2 708.58	4	1	I 2 772.11	6	1
2 577.94	4	3	2 710.55	4	1	2 773.23	4	1
II 2 582.31	4	2 711.66	5	I 2 774.73	4	2
2 582.59	4	4	II+2 714.419	6	5	I+2 778.225	6	1
2 584.54	4	1	2 714.88	4	2 778.85	4	1
II 2 585.88	7	10	2 718.45	4	1	2 779.30	3	4
2 587.96	3	2 719.04	7	2	I 2 781.80	4	1
+2 588.006	5	3	2 719.43	4	2	2 783.69	3	5
II 2 591.55	4	4	I 2 720.91	7	2	2 787.94	4
2 592.80	4	4	I 2 723.58	6	2	2 788.11	6	2
2 598.38	7	8	2 724.89	3	3	2 789.81	3	1
II 2 599.40§S ₁₂	6	10	2 724.96	4	2 791.79	3	1
2 599.57	3	2 726.06	4	1	2 797.78	4	1
2 606.83	5	2 726.24	3	1	2 804.52	7	1
2 607.10	7	10	2 727.39	3	2	2 806.99	7	2
II 2 611.88	8	10	2 727.54	5	6	I+2 813.290	9	2
2 613.84	8	8	2 728.03	4	1	2 823.28	7	2
2 617.62	6	6	2 730.74	4	3	2 825.56	6	1
2 618.03	4	1	I 2 733.58	9	2	I 2 825.69	4	1
2 619.08	3	2	2 734.01	4	1	I 2 827.80	4	1
2 620.42	3	2	2 734.27	4	1	2 831.56	3	4
2 620.70	3	2	I 2 735.48	8	2	2 832.44	6	1
2 621.67	6	4	II 2 736.97	4	4	2 838.12	6	1
2 623.54	4	1	I 2 737.31	6	1	2 843.63	5	1
2 625.50	4	3	II+2 739.550N ₁	9	10	2 843.97	7	2
II 2 625.68	8	4	I 2 742.26	4	1	2 845.60	4	2
+2 628.296	6	8	I 2 742.41	6	1	2 848.72	4	1
I 2 629.60	5	3	II 2 743.20	6	8	+2 851.80	8	2
2 630.08	3	2	I 2 744.07	8	1	I 2 858.90	4
2 631.05N ₂	6	4	2 744.53	5	1	2 863.43	4	1
2 631.33	6	3	II 2 746.49	7	10	I 2 863.87	5	1
2 632.25	4	1	II 2 746.99	7	8	2 866.63	4	1
2 635.82	4	1	2 749.18	4	I 2 869.31	6	1
2 641.65	3	1	II 2 749.32	7	10	2 872.34	4	3
2 651.72	3	1	I 2 750.15	6	2	I+2 874.176	7	1
2 656.15	3	1	2 750.87	4	2 877.30	5	1
2 664.67	3	4	2 753.29	4	5	2 880.76S ₁₁		
2 666.64	3	4	2 753.60	4	1	2 887.81	4	1
2 666.82	4	I 2 754.03	4	1	2 894.51	4	1
+2 679.065	6	2	II 2 755.74¶LS ₁₃	8	10	2 895.04	4	1
2 681.59	4	I 2 756.33	5	1	2 899.42	4	1
2 684.76	3	4	2 757.32	4	1	I+2 912.157	8	2
2 689.22	5	2	2 759.82	4	1	2 918.03	5	2
2 689.84	4	1	I 2 761.79	5	2	2 923.85S ₁₃	4
2 692.61	3	4	2 761.81	4	II 2 926.58S ₁₅	7	3
2 694.54	4	I 2 762.03	5	1	I 2 929.01	7	1
2 696.00	4	2 763.11	4	1	I 2 936.90	7R	2
2 696.29	5	2 764.33	4	1	2 937.81	6
2 699.11	4	1	I 2 766.91	4	1	I+2 941.347	8	3

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
IRON (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 944.40S ₁₇	4	4	I 3 067.25	5	3	3 227.82	4	5
2 947.66	4	4	3 068.18	4	1	3 228.26	4	1
I 2 947.88	5	3	I +3 075.725	5	3	3 233.06	5	2
2 948.44	4	1	I 3 083.75	4	3	3 233.98	6
2 950.25	6	1	I 3 091.58	4	2	3 234.62	5	1
I 2 953.94	4	2	I 3 099.90	4	I 3 236.23	5	1
I 2 957.37	5	2	I 3 099.97	4	4	3 239.44	8	2
2 960.00	4	2	I 3 100.31	4	2	3 244.19	8	2
I 2 965.26	5	2	I 3 100.67	4	3	3 246.97	4	1
I 2 966.90	6R	3	I 3 116.64	5	1	3 248.21	6	1
I 2 969.48	4	2	3 119.50	4	1	3 251.24	5	1
I 2 970.11	4	2	3 120.44	4	1	3 254.37	4	2
I 2 973.14	4	2	I +3 125.661	6	2	3 257.60	4	1
I 2 973.24	4	2	3 129.34	4	3 264.52	4	1
I 2 981.45	4	2	I 3 134.11	5	1	3 265.05	3	1
II 2 984.83	4	6	3 142.45	4	1	3 265.62	6	2
I +2 987.293	5	1	3 142.89	4	1	3 268.25	4
2 990.40	4	1	3 143.99	6	1	+3 271.003	6	2
I 2 994.44	6R	3	3 151.35	6	1	3 280.27	5	1
2 999.52	5	2	3 157.04	4	1	3 282.90	4	1
3 000.45	4	1	3 157.88	4	1	3 284.59	4	1
I 3 000.95	5	2	3 160.66	6	1	3 286.76	8	3
3 007.15	4	1	3 161.95	5	1	3 290.99	4	1
I 3 007.29	4	1	3 166.44	4	1	3 292.03	5	1
3 008.15	5	2	3 171.35	4	1	3 292.60	5	1
I 3 009.58	5	2	+3 175.449	6	1	3 298.14	5	1
3 011.49	4	1	3 178.01	6	1	3 305.98	5	3
I 3 017.63	5	2	3 180.23	8	2	3 306.36	8	3
I 3 018.99	5	2	I 3 180.77	4	3 314.75	6	1
I 3 020.50	5	2	3 181.53	4	1	+3 323.739	4	1
I 3 020.65**	6R	3	I 3 184.90	4	1	3 328.87	4	1
I 3 021.08S ₁₉	6R	3	3 188.84	5	1	3 337.67	4	1
I 3 024.04	5	2	3 191.66	5	1	3 341.91	4	1
3 025.64	4	2	3 192.81	5	2	3 347.93	4	1
I 3 026.85	5	2	3 196.94	4	2	3 355.23	4	1
I 3 026.47	6	2	I 3 199.53	6	1	+3 370.787	6	2
+3 030.152	4	2	3 200.48	6	1	3 378.68	4	1
3 031.22	4	2	3 205.40	7	1	3 379.02	4	1
I 3 031.64	5	2	3 210.25	4	1	3 380.115	5	1
I 3 037.39	5	3	3 210.84	5	1	3 383.70	4	1
3 040.43	4	2	3 211.70	4	1	3 383.99	5	1
I 3 041.75	4	2	3 212.00	4	2	3 392.31	4	2
I 3 042.03	4	1	II 3 213.32	4	2	3 392.657	5	2
I 3 042.67	5	2	3 214.05	8	2	3 394.59	4	1
3 045.09	4	3 215.94	5	2	I 3 396.982	3	1
I 3 047.61	6	3	3 217.39	4	1	+3 399.337	6	2
3 053.07	4	1	3 219.58	5	I 3 401.523	4	1
3 055.27	4	3 219.82	4	3 402.261	4	1
I 3 057.45	5	3	3 222.07	6	3	3 404.35	6	2
I 3 059.09	5R	3	+3 225.790	8	3	3 407.465	7	4
3 067.12	4	II 3 227.76	4	5	3 413.136	7	3

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TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 IRON (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
°3 417.845	6	2	°3 545.64	5	1	3 682.24	6	3
°3 418.511	5	2	3 553.74	5	2	I 3 683.06	4	2
3 422.66	4	2	3 554.93	8	4	°3 684.113	5	2
°3 424.288	6	2	+°3 556.882	6	2	3 686.00	5	2
I 3 426.39	4	1	I+°3 558.18	5	4	I °3 687.400	6R	4
3 426.64	6	1	I °3 565.382	6R	5	3 689.46	6R	4
°3 427.124	6	4	3 568.98	4	1	°3 690.732	2
3 428.20	6	2	I 3 570.10	7R	10	3 694.00	6	2
I 3 440.618 _{uo}	7R	4	3 570.24	7	°3 695.055	3	2
I 3 440.99	6R	4	3 572.00	7	2	3 701.09	6	2
3 442.37	4	1	°3 576.761	4	1	°3 702.035	1
I 3 443.88	6R	3	°3 581.196†	8R	10	°3 704.464	5	2
+°3 445.153	4	2	°3 582.202	4	2	I °3 705.569	6R	4
°3 447.282	6	1	°3 584.664	5	2	°3 707.051	3	1
°3 450.334	6	1	3 584.96	5	2	3 707.83	3
3 451.92	6	1	I °3 585.322	6	3	3 707.92	5	4
I 3 452.28	4	1	I 3 585.71	5	3	3 709.25	6	4
°3 458.307	3	1	°3 586.116	5	3	°3 711.227	2
3 459.92	4	1	I 3 586.99	6	3	°3 715.916	2
I °3 465.864	6R	3	I °3 589.109	4	1	3 716.45	6
3 468.85	4	1	°3 589.45	3	1	I °3 719.936PS _m	8R	10
I 3 475.46	6R	3	°3 594.635	5	3	I °3 722.566	6R	4
3 475.65	4	°3 603.207	5	3	+°3 724.38	6	2
I °3 476.706	5	3	3 605.46	5	3	I °3 727.623	6R	5
I 3 483.01	4	1	+°3 606.682	5	4	°3 732.400	6	1
+°3 485.343 _{u1}	6	1	°3 608.863	6R	6	I °3 733.320	6R	3
°3 489.674	4	1	3 612.08	4	1	I °3 734.866†	9R	10
I 3 490.58	6R	4	°3 617.792	6	3	I °3 737.14p	7R	6
°3 495.290	4	2	I °3 618.771	6R	6	°3 738.310	4	2
°3 497.111	4	2	°3 621.465	6	3	°3 742.624	1
I 3 497.844	5	3	3 622.01	6	3	3 743.47	4	6
°3 506.501	5	1	°3 623.189	5	2	I °3 745.564p	7R	5
I+°3 513.821	5	3	°3 625.149	4	1	I °3 745.904P	6	4
I °3 521.265	5	3	°3 630.353	3	1	I °3 748.265p	6R	4
3 524.08	4	1	3 631.10	5	1	I °3 749.489	8R	10
3 524.24	4	1	I °3 631.467	6R	6	I+°3 753.615	5	2
I 3 526.62	4	2	°3 632.043	6	2	°3 756.943	3	1
I 3 526.17	5	2	3 634.34	5	1	I °3 758.237	7R	8
3 526.38	3	3 637.86	4	1	°3 760.054	5	2
3 526.47	4	1	°3 638.301	6	2	I °3 763.792	6R	6
3 526.67	5	1	+°3 640.392	6	3	°3 765.544	6	3
3 527.80	4	1	°3 645.826	4	2	I °3 767.196	6R	5
°3 529.820	4	1	I °3 647.845	6R	6	°3 774.827	2
3 530.38	4	1	°3 649.510	6	3	°3 776.459	2
3 533.01	4	1	°3 651.473	6	3	°3 781.191	1
3 533.20	5	2	3 655.47	4	1	°3 785.951	5	2
3 536.56	6	3	°3 659.521	5	1	I °3 786.681	3	2
3 537.73	4	1	°3 669.524	6	2	°3 787.883	6R	4
3 540.13	4	1	+°3 670.314	4	1	°3 790.090	4	2
°3 541.087	6	3	+°3 677.630	6	2	°3 794.342	3	1
°3 542.080	6	3	I °3 679.917	5	3	I °3 795.005	6	5

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TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
IRON (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
°3 797.518	5	3	I °3 917.185	5	2	°4 120.210	2
I °3 798.514	6	4	3 918.65	4	1	°4 121.805	2
°3 799.550	6	5	I °3 920.260	6	4	°4 122.519	2
+°3 805.346	6	3	I °3 922.914	6R	4	°4 127.611	4	1
°3 806.702	6	3	°3 925.945	3	1	I °4 132.060	7	4
I °3 807.540	4	2	I °3 927.921	6	4	+°4 132.902	3	2
I 3 812.97	6	4	I °3 930.299	7R	4	+°4 134.680	5	2
°3 814.527	2	°3 932.631	3	1	°4 137.000	3	1
I °3 815.843	7R	10	+°3 935.816	4	1	°4 143.418	5	3
I 3 820.43	8R	10	°3 937.331	2	I °4 143.870	7	5
°3 821.161	6	3	I+°3 940.882	4	1	I+°4 147.073	4	1
I °3 824.445	6R	5	°3 942.443	3	1	°4 154.501	4	2
I °3 825.885	8R	8	°3 948.778	4	2	°4 154.82	4	2
I °3 827.826	6R	8	3 949.96	4	2	+°4 156.803	4	2
°3 833.313	4	1	3 951.17	4	2	°4 170.904	2
I °3 834.225	7R	6	°3 952.605	4	1	+°4 175.639	4	2
°3 839.260	5	2	°3 956.459	4	2	°4 177.596	2
I °3 840.440	6R	4	°3 956.680	6	3	°4 181.758	6	4
I °3 841.052	6R	5	I °3 966.066	5	2	+°4 184.894	4	2
+°3 843.261	5	2	°3 967.423	4	2	°4 187.05	6	4
°3 846.805	5	I °3 969.26	7	5	°4 187.81	6	4
I °3 849.971	6	4	°3 971.325	4	1	+°4 191.436	6	3
I+°3 850.820	5	2	+°3 977.744	5	2	°4 198.31	6	3
I °3 852.577	3	2	°3 981.774	3	1	°4 199.10	6	5
I °3 856.373	6R	5	°3 983.960	5	2	I °4 202.030	7	6
3 859.22	5	2	°3 986.176	3	1	+°4 203.957	3	1
°3 859.914FS ₃₃	7R	6	°3 997.395	6	3	°4 210.36	6	3
I+°3 865.527	6	4	3 998.06	5	2	°4 213.049	2
°3 867.220	3	2	I °4 005.240	7	0	°4 216.188	4	1
°3 871.752	2	°4 009.716	5	2	+°4 219.364	5	3
I °3 872.505	6	4	°4 014.534	4	2	°4 222.22	5	2
°3 873.764	4	2	+°4 021.870	5	2	°4 225.40	4	1
I °3 878.022	6	4	°4 031.964	2	°4 226.423	2
I °3 878.575	6R	5	°4 044.614	2	°4 227.44	7	4
3 878.66	4	I °4 045.816§§	8R	10	+°4 233.609	6	3
°3 883.286	2	°4 062.486	4	2	°4 233.95	8	4
°3 884.362	2	I °4 063.60 §§	8R	10	°4 238.82	4	2
I °3 886.286S ₂₄	7R	5	°4 066.979	4	1	+°4 243.260	2
I °3 887.051	6	3	°4 067.275	3	1	°4 247.44S ₂₃	5	2
I °3 888.518	7	4	°4 067.983	5	1	°4 250.13	7	4
3 891.93	4	1	I °4 071.74	7	8	I °4 250.789S ₂₇	8	6
3 893.40	4	2	+°4 074.789	3	1	°4 260.48S ₂₃	10	10
I °3 895.658	5	3	+°4 076.638	5	2	°4 267.830	2
3 897.90	4	2	°4 085.008	2	I °4 271.764*§§	8	10
I °3 898.01	4	2	+°4 095.973	3	1	+°4 282.406S ₁₀	6	8
I °3 899.709	6	4	°4 098.183	3	1	I °4 294.128S ₂₁	6	4
I °3 902.950	7	5	°4 100.740	2	°4 298.041	2
°3 903.902	3	1	°4 107.492	5	2	°4 299.24	7	4
I+°3 906.482	5	3	°4 109.806	4	2	°4 305.455	2
+°3 907.937	3	1	°4 114.449	4	1	I °4 307.907***	8	10
°3 910.847	2	+°4 118.549	6	3	I+°4 315.087	5	3

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TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 IRON (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 4 325.764†††	9	10	°4 673.168	3	1	°5 166.286	3	1
°4 327.099	2	4 678.86	5	2	+°5 167.49	8	4
I °4 337.050	5	2	+°4 691.414	4	2	I °5 168.901	3	1
°4 346.559	2	I+°4 707.282	5	2	II 5 169.03	2	5
°4 351.550	3	I+°4 710.287	3	1	I °5 171.599	7	2
+°4 352.738	4	2	I+°4 733.596	3	1	I 5 191.46	7	2
°4 358.505	2	+°4 736.782	5	3	I+°5 192.353	8	2
°4 367.583	2	+°4 741.533	3	1	I 5 194.95	5	1
°4 369.776	3	2	°4 745.805	3	1	I °5 198.712	4	1
+°4 375.933	5	2	I+°4 772.818	3	1	I+°5 202.339	5	1
I °4 383.549†††S ₂₂	10	10	°4 786.809	3	1	I+°5 216.227	5	1
°4 387.888	2	°4 788.759	2	°5 227.189	8	4
°4 390.955	3	1	+°4 789.654	3	2	I+°5 232.948	8	5
I °4 404.753§§§	8	10	°4 802.881	2	°5 242.492	3	1
°4 407.715	2	I+°4 859.749	2	2	I+°5 250.650	3	1
I °4 408.419	4	1	I 4 871.33	8	4	I+°5 266.504	8	3
I °4 415.126	8	10	I 4 872.15	6	3	I °5 269.537	10	8
°4 422.572	4	2	I+°4 878.219	5	2	+°5 270.36	8	4
+°4 427.313	5	2	I 4 890.77	7	4	I 5 281.80	5	2
I °4 430.620	4	1	I 4 891.50	9	5	I 5 283.63	7	2
°4 435.153	2	I+°4 903.32	5	2	I+°5 302.309	5	2
I °4 442.345	5	2	I+°4 919.001	8	4	°5 307.361	2
°4 443.197	3	2	I 4 920.52	10	8	I+°5 324.187	6	5
I °4 447.723	5	2	+°4 924.770	3	1	I 5 328.04	7	0
°4 454.384	3	2	I 4 938.83	5	1	+°5 328.534	4	2
I °4 459.122	5	3	I+°4 939.691	3	1	°5 332.901	2
°4 461.655S ₂₂	4	2	I 4 957.31	7	3	+°5 341.026	5	2
+°4 466.556	5	3	I 4 957.61	10	8	I+°5 371.493	7	0
4 469.39	4	3	+°4 966.099	5	1	5 383.37	5	6
°4 476.022	7	4	4 983.86	4	1	I °5 397.132	6	0
I 4 482.26	4	4	I+°4 994.13	3	1	I+°5 405.779	6	0
4 489.742	3	1	+°5 001.872	5	2	5 415.19	4	6
°4 490.085	2	I 5 006.13	5	2	5 424.06	4	8
I °4 494.568	4	I+°5 012.072	4	2	I °5 429.700	6	6
°4 514.190	2	°5 041.074	3	1	I+°5 434.527	6	5
°4 517.528	2	I+°5 041.759	3	1	I °5 446.920	6	6
I °4 528.619	7	6	I+°5 049.825	5	2	I+°5 455.613	6	6
I+°4 531.152	5	2	I °5 051.637	4	1	I 5 473.91	3	1
+°4 547.85	3	2	I 5 079.23	3	1	I+°5 497.520	4	2
°4 587.134	2	I 5 079.74	3	1	I °5 501.469	4	2
I °4 592.655	4	2	I+°5 083.343	4	1	5 563.61	3	1
I+°4 602.945	3	2	I °5 098.704	7	1	I+°5 569.626	5	2
I 4 607.66	4	1	I 5 107.65	4	1	I 5 572.85	5	3
4 611.29	4	2	+°5 110.414	4	1	I 5 576.10	4	1
°4 619.296	4	1	I+°5 123.723	4	1	I+°5 586.763	6	4
°4 630.26	3	4	I °5 127.364	3	1	5 598.30	3	1
I °4 632.915	3	1	5 133.68	5	2	I+°5 615.652	6	4
°4 638.017	4	1	I 5 139.27	6	2	I 5 624.55	5	1
I °4 647.437	4	2	I 5 139.48	8	3	I+°5 658.825	4	1
I °4 654.502	4	I+°5 150.843	4	1	5 701.55	3
°4 667.458	4	2	I °5 151.914	3	1	I 5 709.39	3	1

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TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 IRON (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
5 717.85	3	I+°6 430.852	5	1	+ 7 187.341	10
5 731.77	3	°6 462.733	4	I+ 7 207.422	10
+5 763.013	4	1	°6 475.633	3	+ 7 219.690	2
5 862.35	4	°6 494.987	5	3	+ 7 223.670	2
5 883.84	4	°6 518.376	3	I+ 7 239.896	4
5 914.16	6	1	°6 546.247	5	1	+ 7 284.843	2
5 930.17	5	6 569.23	5	I+ 7 288.764	4
5 934.68	4	1	°6 575.023	3	I+ 7 293.073	6
5 952.74	4	1	+°6 592.920	5	1	+ 7 307.938	3
+6 024.065	4	2	°6 609.118	4	+ 7 311.103	4
+°6 065.489	4	2	°6 663.447	4	+ 7 320.694	3
°6 127.913	2	+°6 677.994	5	+ 7 386.394	4
+°6 136.620	4	3	+ 6 703.573	2	I+ 7 389.423	7
+°6 137.697	4	3	+°6 750.157	4	+ 7 401.691	2
°6 157.730	2	1	+ 6 752.724	3	I+ 7 411.184	8
°6 165.364	2	1	+ 6 806.85	2	+ 7 418.676	3
I °6 173.340	3	1	+ 6 828.612	4	+ 7 443.031	1
+°6 191.563	5	3	+ 6 841.355	5	I+ 7 445.778	9
°6 200.319	2	+ 6 843.676	4	+ 7 491.678	2
I 6 213.44	3	1	+ 6 855.179	6	I+ 7 495.092	8
°6 219.287	3	1	+ 6 885.772	4	+ 7 507.300	2
+°6 230.730	5	3	+ 6 916.709	4	+ 7 511.047	9
6 246.34	4	1	+ 6 933.628	2	+ 7 531.178	4
°6 252.563	4	2	+ 6 945.211	7	+ 7 546.177	2
°6 254.263	3	1	+ 6 951.271	3	I+ 7 568.93	4
I+°6 265.14	4	1	+ 6 978.857	7	+ 7 583.801	4
I °6 297.799	3	+ 6 988.531	2	+ 7 586.050	7
I 6 301.52	5	1	I+ 6 999.912	4	+ 7 620.538	3
+°6 318.024	4	1	I+ 7 022.976	3	+ 7 653.783	2
°6 322.692	3	I+ 7 038.255	4	+ 7 661.230	3
I+°6 335.338	4	1	+ 7 068.418	5	+ 7 664.306	4
6 336.84	4	1	I+ 7 090.41	6	+ 7 710.397	3
°6 344.157	2	+ 7 107.464	2	+ 7 748.282	4
°6 380.749	3	+ 7 112.178	2	+ 7 780.594	5
+°6 393.606	5	2	I+ 7 130.946	10	+ 7 832.233	6
6 400.02	5	3	+ 7 132.996	3	I+ 7 937.172	9
6 408.04	4	I+ 7 164.472	9	+ 7 945.882	7
6 411.67	5	1	+ 7 181.222	3	I+ 7 998.980	6
°6 421.357	4	1						

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TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
IRON (Continued)

Control lines:	Interfering lines:		
*As 2370.8	*Pt Te Ti		
Co 2378.6			
†Ni 2416.1	†Ag Mo Pb		
†Sn 2421.7	†Bi Cu Hg Mo		
§Sb 2528.5	§Pb Sb		
AuC3122.8	Au Cd Cr Pt		
Cr 2750.7			
¶Cr 2750.7	¶Ag Ge V W		
**Bi 2989.0	**Cr Hg Mo V W		
Cr 2605.3			
††Mo 3624.5	††Au Ba Mo Pd		
††Ca 3179.3	††Ca Co Cu Mo		
Ti 3752.9			
§§Co 4092.4	§§Co Cr Hg K Ni Pt		
K 4044.2			
Mn 4055.6			
Co 4086.3	As Au Co Cu Ni Pb		
Cu 4651.2			
¶¶Cr 4254.3	¶¶Be Bi Co Cr Pt Ti		
Ti 4337.9			
***Ca 4318.6	***Ba Bi Ca Cd Co Ni Pt		
Ti 4533.2	Sr Ti		
†††Mo 4288.7	†††Ba Be Co Cr Na Ni Pt		
V 4323.8			
4371.3	†††Al Bi Cr Mn Mo Pt Se		
Mo 4385.9			
Pb 4245.2			
4374.5	. Ba Co Cr Mo Te Ti		
V 4111.8	V W		
Control lines:		Control lines:	
B ₁ Co 2378.6		S ₁₅ Cu 3036.1	
S ₁ Cu 2356.5			3073.8
2406.7		S ₂₀ Cu 3454.7	
S ₂ Cu 2406.7		S ₂₁ Cu 3478.2	
2473.5		S ₂₂ Sr 4607.3	
S ₃ Cu 2406.7		S ₂₃ Sr 4607.3	
2516.1		S ₂₄ Sr 4607.3	
S ₆ Si 2516.1		S ₂₅ Sr 4607.3	
2516.1		S ₂₆ Mn 4254.3	
2516.1		S ₂₇ Mn 4254.3	
S ₈ Si 2516.1		S ₂₈ Mn 4277.8	
S ₉ Si 2516.1		S ₂₉ Mn 4254.3	
S ₁₀ Si 2528.5		Sr 4607.3	
S ₁₁ Si 2524.1		S ₃₀ Mn 4254.3	
S ₁₂ Cu 2600.4		4289.7	
S ₁₃ Cu 2703.3		S ₃₁ Mn 4289.7	
S ₁₄ Si 2881.6		S ₃₂ Sr 4607.3	
S ₁₅ Mn 2933.1		S ₃₃ Sr 4607.3	
2939.3		N ₁ Sn 2380.7	
S ₁₆ Si 2881.6		N ₂ Sn 2523.9	
S ₁₇ Mn 2949.2		2455.8	
		N ₃ Sn 2779.3	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

LANTHANUM

La

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 379.4L	10	4 287.0	8	10	5 501.4	6R	1
3 171.7	10	4 296.1	9	8	5 541.3	4R
3 245.1	6	4	4 322.5	6	5	5 588.3	4R
3 249.4	5	3	4 333.8L	10	10	5 648.3	5
3 265.7	6	4	4 335.0	6	8	5 740.7	6R	1
3 303.1	6	5	4 354.4	8	10	5 744.4	5R
3 337.5	8	10	4 378.1	7	4	5 761.8	5R	1
3 344.6	8	7	4 383.5F	6	8	5 769.1	7R	3
3 380.9	8	10	4 385.2	5	4	5 769.4	7R	1
3 517.1	10	4 423.9F	4	2	5 770.0	5R
3 645.4	6	8	4 427.6	7	8	5 789.2	6R	1
3 650.2	5	4	4 429.9L	10	10	5 791.3	7R	1
3 713.6	5	6	4 452.2	6	1	5 797.6	7R	2
3 715.5	5	4	4 522.4	9	10	5 805.8	5R	5
3 759.1	8	10	4 525.3	6	8	5 808.3	5R	1
3 790.8	8	10	4 526.1	8	8	5 822.0	6R	1
3 794.8	8	10	4 549.5	6	1	5 823.8	4R
3 840.7	5	5	4 558.5	7	5	5 829.7	4R
3 849.0	6	10	4 567.9	6	1	5 845.0	4R
3 871.6	8	10	4 570.0	6	1	5 848.4	4R
3 886.3	7	10	4 574.9	8	5	5 855.6	4R
3 916.0	7	10	4 580.1	6	3	5 863.7	5R	2
3 921.5	7	10	4 613.4	6	5	5 880.6	5R	2
3 929.2	8	10	4 619.8	5	6	5 894.8	4R
3 949.1P	10	10	4 655.5	7	10	5 930.6P	6R	3
3 988.5	10	10	4 662.5	6	4	6 038.6	4R
3 995.8	10	5	4 663.8	5	8	6 068.7	4R
4 025.9	6	4	4 668.9	5	8	6 108.5	5R
4 031.7	7	10	4 671.8	4	5	6 111.7	4R
4 042.9	8	10	4 692.5	5	5	6 126.1	4R	3
4 050.1	6	10	4 728.4	7	3	6 129.6	5R	3
4 067.4	6	8	4 740.3	8	5	6 134.4	5R
4 077.4p	10	10	4 743.1	8	10	6 165.7	5R
4 086.7	10	10	4 748.7	6	5	6 249.9p	7R	5
4 099.6	7	10	4 809.0	6	3	6 262.3	5R	6
4 123.2pL	10	10	4 824.1	6	4	6 266.1	4R	1
4 141.8	10	10	4 860.9	6	3	6 293.6	4R	2
4 152.0	8	10	4 899.9	7	4	6 296.1	5R	5
4 152.8	4	5	4 921.0	7	5	6 320.4	5R	5
4 192.3	7	8	4 921.8	7	5	6 325.9	5R	1
4 196.6	10	10	4 986.8	6	2	6 390.5	5R	7
4 204.0	5	4	4 999.5	6	3	6 394.2	6R	6
4 217.6	6	10	5 106.2	6	1	6 399.0	5	5
4 231.0	4	6	5 114.5	6	3	6 411.0	10	3
4 238.4	10	10	5 123.0	5	3	6 454.5	6	1
4 250.0	5	6	5 183.4	8	5	6 456.0	5R	3
4 263.6	6	8	5 302.0	5	1	6 527.0	8	4
4 269.5	6	10	5 455.1p	6	1	6 543.2	8	1
4 275.6	4	4	5 464.4	5	1	6 578.5	5	3

For explanation of control and interfering line symbols see page 365.

TABLE IV (*Continued*)
 PRINCIPAL LINES BY ELEMENTS
LANTHANUM (*Continued*)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
6 616.6	4	6 753.1	4	7 282.3	5
6 650.8	4	6 774.3	6	3	7 334.2	5
6 661.4	4	1	7 066.2	5	7 345.3	4
6 671.4	4	2	7 068.3	4	7 483.5	4
6 709.5	4	7 161.2	4			

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS

LEAD

Pb

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 059.0	7R	10	2 577.3N ₂	6R	3R	3 683.5p LB ₁ N ₈ Sn	3R	10R
2 060.7	7R	7	2 614.2S ₅ G ₁ N ₂	6R	5R	3 740.0	5R	4R
2 088.2	5R	2 628.3S ₅	2R	2	3 854.0	10
2 115.0	5R	2 657.2S ₄	4 019.6	3	10
2 170.0P	6R	2R	2 663.2G ₂ N ₄	10R	10R	4 057.8p¶FLS ₁₂	5R	10R
2 175.6	4R	2 802.0†G ₂ N ₅	5R	10R	G ₂ N ₅		
2 203.5PN ₁	3	4R	2 823.2G ₄	4R	10R	4 062.2	3	10
2 246.9	6R	4R	2 833.1p†S ₅ N ₆ G ₅	6R	10R	4 168.03	3	10
2 332.5	4R	2	2 873.3S ₇ G ₇	6R	10R	4 242.5	10
2 388.8S ₁	3R	2	3 043.9	1	10	4 245.2	10
2 393.8	5R	3R	3 137.8	10	4 386.0	10
2 401.9	4R	3	3 176.5	10	5 608.8	4	10
2 411.8S ₂	4R	2	3 220.5S ₁₀	4	2	5 895.7	5
2 443.9	4R	4	3 572.7	5R	10	6 002.0	5
2 446.2S ₃	4R	4	3 639.6p‡N ₇	6R	10R	7 229.0	6
2 476.4S ₄	4R	2R						

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Fe 2628.3	*Ag Co Fe V Sb	Mo 3614.3	
Sb 2670.7		Mo 3158.2	
W 2613.1		Sc 3630.8	
†Mg 2795.5	†Au Hg Mg Mn	Ti 3653.5	
Mn 2798.3		Fe 3709.3	Ag Co Fe Hg Pt
V 2810.2		Fe 3705.6	
Zn 3075.9		Mo 3695.0	
†Cr 3605.3	‡Au Fe Hg W	Ti 3234.5	
Fe 2844.0		V 3695.9	
Pt 2929.8		V 3695.3	
W 2848.0		¶Mn 4048.8	¶Ag Co Cr Cu Fe ?
W 2947.0		Mn 4041.4	
‡Ca 3706.0	‡Ba Co Cr Fe Hg Pt		
Control lines:	Control lines:	Control lines:	
S ₁ Sn 2706.5	S ₁₂ Cu 4062.8	N ₄ Zn 2670.4	
S ₂ Sn 2421.7	G ₁ Sn 2594	N ₅ Sn 2787.9	
S ₃ Cu 2406.7	2637	2790.2	
S ₄ Cu 2406.9	G ₂ Sn 2661	2761.8	
S ₅ Cu 2618.4	G ₃ Sn 2851	N ₆ Sn 2761.8	
S ₆ Sn 2571.6	2765	N ₇ Sn 3223.6	
S ₇ Bi 2730.5	G ₄ Sn 2765	3218.7	
2780.5	G ₅ Sn 2851	3655.9	
Sn 2571.6	G ₆ Sn 2765	N ₈ Sn 3655.9	
2706.5	G ₇ Sn 2801	N ₉ Zn 4680.2	
S ₈ Cu 2858.3	3656	4629.9	
2882.8	N ₁ Sn 2209.3	Sn 4524.7	
S ₉ Cu 2858.3	2211.0	3223.6	
2882.8	N ₂ Sn 2558.0	2655.9	
S ₁₀ Bi 3024.6	N ₃ Sn 2594.4	3218.7	
3067.7	2637.0	B ₁ Ni 3619.4	
S ₁₁ Cu 3687.5			

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

LITHIUM

Li

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 425.6	3R	I 3 794.0	5	I 4 603.0†	9R	10
I 2 475.0	4R	I 3 915.0	2R	1	I 4 636.0	3
I 2 562.5	5R	I 3 985.7	3	I 4 971.9	7	4
I 2 741.3	6R	2R	I 4 132.3	5	1	I 6 103.6	10R	10
I 3 232.7p*	8R	3R	I 4 273.3	5	2	I 6 240.6	1
I 3 719.0	3	I 4 602.0	9R	10	I 6 707.9P	10R	10R

Control lines:

Interfering lines:

*Ni 3057.6

*Ag Au Co Fe Mn Ti Tl W

Sb 3267.5

Ti 3361.2

Ti 3222.8

Control lines:

Interfering lines:

Ti 3529.4

†Cr 4616.1

Fe 4482.3

Sr 4215.5

†Al As Ba Be Co Mn Mo Ni

P Pb

LUTECIUM

Lu

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 603.3	10	3 081.5	9	3	3 876.7	10	10
2 615.4	10	10	3 191.8	2	10	4 124.7	10	5
2 657.8	4	10	3 198.1	10	10	4 184.2	10	10
2 754.2	4	10	3 254.3	10	10	4 518.5p	10	5
2 772.6	10	3 279.0	10	4	4 658.0	10	3
2 796.6	4	10	3 281.8	10	5	4 994.1	10	3
2 847.5	5	10	3 312.1	10	5	5 135.1	10	1
2 894.9p	10	10	3 359.6	10	5	5 402.6	10	1
2 900.3	10	10	3 376.5	10	5	5 476.7	10	10
2 911.4p	10	10	3 397.0p	10	10	5 736.5	10	1
2 951.7	3	8	3 472.5p	10	10	5 983.7	10	1
2 963.3	7	10	3 507.4	10	10	5 984.1	10	1
2 969.8	6	10	3 508.4	10	3	6 004.5	10	1
3 020.6	4	10	3 554.4p	10	10	6 221.9	10	4
3 056.7	10	10	3 567.8	10	5	6 463.2	10	3
3 058.0	10	3 624.0	10	10	6 523.2	10
3 077.6	10	10	3 636.26	10	3			

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
MAGNESIUM

Mg

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 026.0	6	6	2 915.5	3	8	II 3 850.4	6
II 2 660.8	5	II 2 928.7	3	10	I 4 167.6	4	1
II 2 660.8	5	II 2 936.6	4	10R	I 4 351.9	8	2
I 2 669.7	6	I 2 936.8	4	II 4 384.6	8
I 2 672.6	8	I 2 938.5	5	II 4 390.6	10
I 2 695.3	4	I 2 942.1B ₂	6	2	II 4 428.0	7
I 2 698.2	5	I 3 091.1	8R	1	II 4 434.0	8
I 2 733.6	4	1	I 3 093.1	8R	2	II 4 481.1	10
I 2 736.6	4	1	I 3 096.9	10R	2	I 4 571.1	5	2
I 2 776.7	6R	6R	II 3 104.7	10	I 4 703.1	10	5
I 2 778.3	6R	6R	II 3 104.8	10	II 4 739.6	5
I 2 779.9	8R	8R	I 3 329.9B ₄	8	3	II 4 851.1	5
I 2 781.4	6R	6R	I 3 332.2	10	5	I 5 167.3	8R	10
2 783.0	6R	6R	I 3 336.7	10	8	I 5 172.7	10R	10
II 2 790.8	4	10R	II 3 535.0	5	I 5 183.6	10R	10
II 2 795.5P*LB ₁	10R	10R	II 3 538.8	6	I 5 528.5	10	5
II 2 798.0	10	I 3 829.4p	8R	10R	I 5 711.1	5	1
II 2 802.7p†LB ₂	10R	10R	I 3 832.2p	10R	10R	II 6 347.1	4
I 2 846.8	4	1	I 3 838.3	10R	10R	II 7 877.1	4
I 2 848.4	5	1	II 3 848.2	7	II 7 896.3	5
I 2 852.1P†L	10R	10R						

Control lines: Interfering lines:

*Mn 2794.8 *Fe Mn Sb
W 2848.0
†Mn 2798.3 †Au Bi Cr Cu Hg
Pb 2833.1 Pb Ti V W Zn
V 2810.2
Zn 3075.9
†Cr 2849.8 †Au Cr Fe Na Sb
Cr 2843.3
Fe 2844.0
Mo 2816.2

Control lines: Interfering lines:

Sn 2546.5
W 2866.1
B₁Cu 2961.2
3036.1
Sn 3262.3
B₂Cu 2824.4
Zn 3075.9
B₂Cu 3247.5
B₁Zn 3345.0

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

MANGANESE

Mn

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
II 2 452.5	2R	10	I 3 488.7	4	10	I 4 414.9	8	6
2 575.5	5	1	I 3 495.8	5	6	I 4 436.4	7	5
II 2 576.1P*L	5R	10R	I 3 531.8	4R	2	I 4 451.6	9	3
2 593.0	5	1	I 3 532.0	5R	3	I 4 453.0	5	3
II 2 593.7p†L	4R	10R	I 3 532.1	5R	3	I 4 455.0	6	3
II 2 605.7p†L	5R	10R	I 3 547.8	5R	4	I 4 455.3	6	3
2 618.2	4	8	I 3 548.0	4R	3	I 4 455.8	5	3
2 625.6	8	I 3 548.2	4R	3	I 4 457.0	5	2
2 632.4	1	8	I 3 569.5	6R	5	I 4 457.6	6	4
2 638.2	1	5	I 3 569.8	8R	4	I 4 458.3	6	5
2 655.8	5	I 3 570.1	4R	3	I 4 461.1	6	4
2 672.6	1	5	I 3 577.9	8R	5	I 4 462.0	9	8
2 695.4	1	5	I 3 586.6	5	5	I 4 464.7	7	5
2 701.7	3	5	I 3 607.5	8	3	I 4 470.1	7	4
2 705.7	2	8	I 3 608.5	6	3	I 4 472.8	7	3
2 711.6	5	I 3 610.3	6	3	I 4 490.1	5	3
I 2 794.8§	6R	5R	I 3 806.9	6	8	I 4 498.9	7	4
I 2 798.3	6R	5R	I 3 809.6	6	6	I 4 502.2	7	4
I 2 801.1¶	6R	5R	I 3 823.5	4R	6	I 4 626.5	5	2
2 879.5	1	5	I 3 823.9	4	4	I 4 700.7	7	2
2 886.7	2	6	I 3 833.9	6	4	I 4 727.5	7	2
2 889.5	3	10	I 3 834.4	6R	8	I 4 739.0	5	2
I 2 914.6	8	1	I 3 839.8	4	5	I 4 754.1	10	8
I 2 925.6	6	1	I 3 841.1	4	6	I 4 761.5	5	2
II 2 933.1G ₁	6	10	I 3 844.0	6	4	I 4 762.4	9	4
II 2 939.3G ₂	6	10	3 985.2	4	3	I 4 765.9	5	2
I 2 940.4	6	1	I 4 018.1	8	8	I 4 766.4	6	3
II 2 949.2S ₁ G ₂	6	10	I 4 030.8P**B ₁	6R	10R	I 4 783.4	10	4
I 3 044.6	4	2	I 4 033.1p††B ₂	8R	10R	I 4 823.5	10	4
I 3 054.4	4	2	I 4 034.5p††B ₃	8R	10R	4 965.9	5	1
I 3 062.1	4	1	I 4 035.7	5R	8	5 196.6	5	1
I 3 079.6	5	1	I 4 041.4	8R	10	5 255.3	5	2
3 110.7	5	1	4 045.2	4	5	I 5 341.1	10	8
I 3 148.2	4	1	I 4 048.8	4	8	5 377.6	8	3
I 3 178.5	8	1	I 4 055.6	8	8	5 394.7	7	2
I 3 212.0	6	2	I 4 079.3R	6	5	5 399.5	8	3
3 228.1	5	3	I 4 079.4	6	5	I 5 407.4	7	2
I 3 236.8	6	3	I 4 083.0	6	6	5 413.7	7	2
I 3 243.8	4	2	I 4 083.6	6	6	I 5 420.4	7	3
I 3 248.5	4	3	4 131.1	4	4	5 432.6	6	1
I 3 250.1	4	2	4 176.6	4	4	I 5 470.6	8	2
I 3 258.4	4	2	4 190.0	4	4	I 5 481.4	6	1
3 317.3	6	1	I 4 235.1S ₂	8	5 505.9	6	1
3 320.7	4	1	I 4 235.3S ₃	8	10	I 5 516.8	8	2
3 330.7	4	3	I 4 239.7	5	5	I 5 537.8	7	2
I 3 442.0L	5	10	I 4 257.7	5	4	5 552.0	5	1
I 3 460.3	3	10	I 4 265.9	5	5	5 567.8	4	1
I 3 474.1	4	10	I 4 281.1	5	5	5 738.3	4
I 3 482.9	4	10	4 374.9	4	2	5 780.2	5

For explanation of control and interfering line symbols see page 365

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
MANGANESE (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 6 013.5	10	1	6 990.0	4	7 302.9	6
I 6 016.6	10	1	7 069.9	4	7 326.6	7
I 6 021.8	10	1	7 151.3	8	7 680.2	5
6 441.0	5	7 184.3	5	7 710.2	5
6 491.7	7	7 247.8	5	7 712.4	5
6 605.6	4	7 283.8	6	7 764.8	5
6 942.6	5						
Control lines:	Interfering lines:		Control lines:	Interfering lines:				
3082.2	*Al Hg Pb W		†Mg 2795.5	†Au Cr Hg Mg Pb Sc Zn				
†Ge 2709.6	†Bi Fe Mo Na Sn		Pb 2833.1					
†Fe 2611.9	†Ag Co Cr Fe Ti		**Ga 4172.1	**Cr Fe Ga Mo Pt Se				
§W 2848.0	§Au Fe Mg Mo Pt V		††Ga 4172.1	††Co Cr Fe Ga Mo Sb				
‖Mg 2779.9	‖Bi Hg Mg Mo Pb		††Ga 4172.1	††Co Fe Ga Mo Ni Pt				
Mg 2802.7								
Control lines:	Control lines:		Control lines:	Control lines:				
SiCu 2858.0			SeCu 4249.0	GaFe 2944.4				
2997.4			SeCu 4249.0	BiFe 4009				
2882.9			GiFe 2923.8	BiFe 4014				
2961.2			GiFe 2923.8	BiFe 4021				

MERCURY

Hg

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
II 2 224.7	4	4	I 3 125.6	8	8R	I 4 358.3†	10	10R
I 2 378.3	3	I 3 131.6	7	5R	I 4 916.0	5	1
I 2 399.3	3	I 3 131.8	7	4R	I 4 960.3	5
I 2 482.7	3	I 3 341.5	6	5	I 5 460.7	10R	10R
I 2 534.8	4	2	I 3 650.2†	10	9R	I 5 675.8	5
I 2 536.5P*L	10R	10R	I 3 654.8p	7	5	I 5 769.6	10	5
I 2 652.0	5	2	I 3 662.9	4	4	I 5 790.7	10	5
2 698.9	3	I 3 663.3	6	5	I 6 072.6	5
I 2 752.8	4	4	I 3 906.4	6	6 123.5	6
I 2 803.5	4	3 984.0	6	8	I 6 234.4	8
II 2 847.7	8	I 4 046.6	10	10R	I 6 907.5	10
I 2 893.6	5	5	I 4 077.8	7	5R	I 7 082.0	4
I 2 967.3B ₁	5	SR	I 4 339.2	6	1	7 729.2	6
I 3 021.5B ₂	5	4	I 4 347.5	6	1			
Control lines:	Interfering lines:		Control lines:	Interfering lines:				
*Fe 2539.0	*Co Fe P Pb Pt W		Sc 2813.7					
Fe 2538.8			Ti 3234.5					
W 2533.0			Ti 3239.0					
Co 2432.2			†Fe 4401.3	†Al Ba Co Cr Fe Mg Ni Pt Se				
Fe 2541.0			Cr 4371.3	Ti V				
Mo 2646.5			B ₂ Sn 3009.1					
Ti 2534.6			B ₂ Sn 2863.3					
†Fe 3631.5	†Cd Cr Fe Mo Se							

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
MOLYBDENUM
Mo

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 538.5	2	10	I 3 798.3P§	10R	10R	4 979.1	5	2
II 2 638.8	3	10	3 833.8	7	3	I 5 172.9	9	1
II 2 644.3	2	10	I 3 864.1p	10R	10	I 5 174.2	9	2
II 2 660.6	2	10	I 3 903.0p¶	10R	10	I 5 238.2	7	3
2 672.8	2	10	II 3 941.5	1	10	I 5 240.9	6	3
II 2 684.1	3	10	3 961.5	3	10	I 5 350.6	10	8
II 2 701.4	2	10	4 069.9	9	8	5 473.4	6	6
2 775.4	3	10	4 084.4	8	3	I 5 506.5	10	10
2 780.0	3	10	I 4 102.2	7	3	I 5 533.0	10	10
II 2 816.2PL	5	10	4 143.6	9	5	I 5 570.5	10	10
II 2 848.2pB ₁	5	10	4 185.8	8	4	I 5 632.5	9	8
2 853.2	1	10	4 188.3	10	5	I 5 650.1	8	6
II 2 871.5p	4	10	4 232.6	10	5	I 5 689.2	9	10
2 903.1	2	10	4 250.7	1	10	I 5 722.8	8	7
II 2 911.9	5	10	4 251.9	10R	2	I 5 751.4	10	10
II 2 923.4	4	10	4 276.9	10	5	I 5 791.8	10	10
3 087.6	2	10	I 4 277.3	10	6	I 5 858.3	8	10
3 110.1	1	8	II 4 279.0	2	10	I 5 888.3	10	10
3 122.0	2	10	I 4 292.2	9	4	I 5 928.8	9	10
I 3 132.6*	10R	2	I 4 293.2	10	4	I 6 030.7	9	10
3 158.2	9R	2	I 4 293.9	9	3	6 357.2	5	3
I 3 170.4†	10R	2	4 326.1	9	4	6 424.4	8	8
I 3 194.0‡	10R	2	II 4 363.7	1	10	6 519.8	4	3
3 208.9	10	2	II 4 377.8	1	10	I 6 619.2	9	8
3 292.3	1	10	4 381.7	10	8	6 650.4	7	1
3 325.7	10	1	4 411.7	10	8	I 6 734.0	7	1
I 3 327.3	10	1	II 4 433.5	1	8	6 746.3	5	1
3 344.8	8	2	4 435.0	10	4	6 839.0	4
3 347.0	6	1	4 468.3	10	2	6 886.4	4
I 3 358.1	9	2	4 491.3	6	2	6 914.1	5
I 3 384.6	8	2	I 4 524.3	7	2	6 989.0	4
3 402.8	1	8	I 4 570.5	8	2	I 7 060.2	4
3 447.1	10	3	I 4 595.2	7	2	I 7 109.9	8
3 504.4	6	2	4 621.4	7	2	I 7 134.1	4
3 524.6	2	7	I 4 626.5	10	4	I 7 242.5	7
3 614.3	8	3	4 707.3	10	5	7 245.9	4
3 635.2	2	10	4 731.5	10	7	I 7 391.4	5
3 651.1	1	8	4 760.2	9	9	I 7 485.7	7
II 3 688.3	1	10	4 819.3	10	4	I 7 656.7	5
II 3 692.7	2	9	4 830.5	10	4	7 720.7	4
II 3 702.6	2	8	4 868.0	5	2			

Control lines:

Interfering lines:

*Be 2348.6
Cr 2849.8
Hg 3650.2
Ni 3012.0
†Ti 3242.0
‡Cr 3180.7
Fe 3222.1
V 3267.7
§Ce 4186.6
Fe 3795.0

*Au Be Cd Cr Fe Sc Te V

†Cu Fe Mn V W

‡Au Cu Fe Mn V

§Cr Fe Mg Pd Sn

Control lines:

Interfering lines:

||Fe 3869.6
Fe 3895.7
Fe 3820.4
¶Fe 3895.7
Fe 3899.7
Fe 3856.4
Si 2519.2
Ti 3948.7
BiCr 2849.8

||Bi Cr Fe Mn Sr

¶Cr Fe Hg Mn

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
NEODYMIUM

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
3 092.9	4	2	4 156.2	10	10	5 620.6	8	5
3 133.6	4	2	4 177.3p	9	10	5 688.5	6	3
3 217.1	4	1	4 178.7	6	3	5 708.3	5	2
3 275.2	4	2	4 232.4	8	5	5 729.3	4
3 300.1	4	2	4 247.4	10	8	5 804.0	5	2
3 328.3	5	2	4 282.5	10	8	6 007.6	4
3 388.0	5	1	4 303.6p	10	10	6 066.1	4
3 410.2	4	1	4 314.5	7	8	6 071.7	4
3 543.3	5	2	4 325.8	10	5	6 074.0	4
3 592.6	5	2	4 327.9	7	5	6 178.6	4	1
3 609.8	5	1	4 351.2	9	8	6 310.5	7	1
3 653.1	6	2	4 358.2	9	8	6 341.5	7	2
3 735.6	7	5	4 375.0	10	6	6 385.2	8	3
3 780.4	5	3	4 385.7	10	8	6 485.7	4	1
3 851.7	8	5	4 400.8	10	5	6 630.2	4
3 863.4	10	8	4 411.0	8	5	6 650.6	4	1
3 875.9	6	2	4 446.4	10	10	6 655.7	4
3 890.0	6	3	4 451.6	10	10	6 740.1	4
3 890.6	6	4	4 463.0	10	10	6 790.4	4
3 891.0	7	4	4 501.8	7	5	6 804.0	4
3 892.1	6	4	4 541.3	5	5	6 846.7	5
3 894.7	6	3	4 563.2	6	5	7 037.3	4
3 900.3	6	6	4 579.3	5	4	7 068.9	4
3 905.9	7	4	4 634.2	5	3	7 129.4	4
3 941.5	7	8	4 706.5	7	4	7 189.4	4
3 951.2p	9	8	4 811.3	5	5	7 418.2	4
3 963.1	7	6	4 825.5	8	8	7 448.7	4
3 990.1	9	6	4 859.0	5	5	7 511.2	4
3 994.7	8	5	4 920.7	9	3	7 513.8	4
4 012.3	9	10	5 192.6	6	3	7 529.0	4
4 021.8	7	3	5 249.5	7	4	7 538.3	4
4 062.1L	10	10	5 293.2	9	5	7 696.6	4
4 069.3	5	4	5 319.8	9	4	7 808.5	4
4 075.2	7	2	5 361.5	5	4	7 862.8	4
4 109.1L	8	6	5 431.5	4	3	7 958.9	4
4 109.5L	9	8	5 485.7	7	4	7 965.7	4
4 135.3	9	7	5 594.4	8	5	7 982.3	4

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

NICKEL

Ni

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 019.0	6	I 3 413.5	5R	3	I 5 017.6	7	2
2 021.0	6	I 3 414.8P†B ₁	10R	10	I 5 035.4	10	3
2 029.1	6	I 3 423.7	8R	5	5 080.5	8	3
I 2 320.1	5R	1	I 3 433.6L	9R	6	5 081.1	9	3
I 2 325.8	3R	2	I 3 437.3	6R	5	5 084.1	6	1
I 2 345.5	2R	8R	I 3 446.3	10R	10	I 5 100.0	7	1
2 375.4	1	8	I 3 452.9	6R	5	I 5 115.4	9	2
2 394.6L	2	10	I 3 458.5	10R	10	I 5 125.2	7
2 416.1L	1	10	I 3 461.7‡	10R	10	I 5 129.4	8	1
2 437.9	1	10	I 3 472.6	7R	5	I 5 137.1	8	1
2 510.9	4	10	I 3 483.8	6R	4	I 5 142.8	10	2
2 545.9	1	6	I 3 493.0p B ₂	10R	10	I 5 146.5	10	2
I 2 798.7	4	1	3 500.9	6	4	I 5 155.8	9	1
I 2 821.3	4	2	I 3 510.3	7R	10	I 5 168.7	8	1
I 2 943.9	6	2	I 3 515.1p†B ₃	9R	10	5 176.6	6	1
I 2 981.7	7	3	I 3 524.5p**	10R	10	5 411.2	6	1
I 2 992.6S ₁	6	2	I 3 566.4	10R	10	I 5 435.9	7	1
I 2 994.5	7R	3	I 3 571.9	7R	3	I 5 476.9	10	10
I 3 002.5*	10R	5	I 3 597.7	8R	6	I 5 592.2	7	2
I 3 003.6	9R	4	I 3 610.5	9	4	I 5 593.7	6	1
I 3 012.0S ₂	9R	5	I 3 619.4†LB	10	10	I 5 614.8	6	1
I 3 037.9	9R	4	I 3 674.1	6	3	5 625.3	7	1
I 3 050.8†S ₃	10R	6	I 3 722.5	6	1	5 682.2	7	1
I 3 054.3	8R	4	I 3 736.8	6	3	5 695.0	7	1
I 3 057.7	10R	4	I 3 775.6	8	5	I 5 709.6	8	2
I 3 064.6	6	2	I 3 783.5	8	5	I 5 715.09	8	1
I 3 080.8	6	2	I 3 807.1	8	8	I 5 754.67	6	1
I 3 097.1	5	2	I 3 831.7	6	2	I 5 760.84	6	1
I 3 101.6	9R	4	I 3 858.3	10	8	I 5 805.20	10
I 3 101.9	9R	3	I 4 401.6	10	8	5 831.60	8
I 3 134.1S ₄	10R	4	I 4 459.0	9	8	I+5 857.759	10	1
I 3 197.1S ₅	5	2	I 4 462.5	8	3	I+5 892.88	9	1
I 3 221.7	4R	2	I 4 470.5	9	3	I 6 086.3	10	1
I 3 225.0	5R	2	I 4 592.5	9	4	I 6 108.1	7	1
I 3 232.9	8R	3	I 4 600.4	8	1	I 6 116.2	9	1
I 3 234.7	5R	2	I 4 605.0	9	3	6 163.4	8	1
I 3 243.1	8R	3	I 4 648.7	10	3	I 6 175.4	10	1
I 3 315.7	7R	3	I 4 686.2	5	3	6 176.8	10	2
I 3 320.3	5R	3	I 4 714.4	10	8	I 6 186.8	7
I 3 351.6	5R	3	I 4 715.8	8	3	I 6 191.2	7	1
I 3 365.8	4R	3	I 4 756.5	7	3	I 6 224.0	6
I 3 366.2	5R	3	I 4 786.5	10	3	I 6 256.4	7	1
I 3 369.6	10R	4	I 4 829.0	8	3	I 6 314.7	10
I 3 372.0	5R	3	I 4 831.2	5	3	I 6 339.2	10
I 3 374.2	4R	2	I 4 855.4	8	3	I 6 378.2	7
I 3 380.6	10R	6	I 4 866.3	7	2	I 6 384.7	7
I 3 380.9	4R	2	4 904.4	9	3	6 421.5	7
I 3 391.1	7R	4	4 980.2	9	2	I 6 482.8	7	1
I 3 393.0	10R	8	I 4 984.1	9	2	I 6 586.3	6

For explanation of contro land interfering line symbols see page 305.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
NICKEL (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 6 598.5	6	I 6 767.8	10	I 6 914.6	7
6 635.1	6	I 6 772.4	9	I 7 024.8	8
I 6 643.7	10	1	I 6 842.1	6	I 7 122.3	10

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Cr 3024.4	*Au Cu Fe Mn Mo V W	Mn 3442.0	
Fe 2994.4		Co 3409.2	Co Cr Mo Ti V W
†Cr 3030.3	†Al Co Cr Fe Hg Mg	Fe 3475.5	
Fe 2994.4		¶Co 3409.2	¶Be Co Fe Mo Pt Ti
‡Co 3409.2	‡Co Cu	**Co 3506.3	**Au Ba Co Cu Fe Hg Mo
§Cd 3610.5	§Cd Co Mn Ti V W	Fe 3558.5	Tl V W
Co 3474.0		††Fe 3631.5	††Cr Cu Fe Mn Ti V
Control lines:	Control lines:	Control lines:	Control lines:
SiCu 2997.4	3142.4		BiFe 3415
SiCu 3010.8	3126.1		BzFe 3495
SiCu 3063.4	SiCu 3208.2		BzFe 3516
SiCu 3140.4			

OSMIUM

Os

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 838.6L	5	3	3 850.0	10	4 865.6	10
2 909.1*	7	5	3 857.1	10	5 149.7	7
3 058.7†	7	4	3 876.8	7	3	5 416.3	10
3 156.3	7	3	3 963.6	10	3	5 523.6	10
3 267.9p	8	3	3 977.2	10	3	5 584.4	10
3 391.6p‡	9	2	4 066.7	10	3	5 721.9	10
3 370.6	7	2	4 091.8	9	2	5 780.8	10
3 528.6	9	3	4 112.0	10	4	5 857.6	10
3 559.8	9	3	4 135.8	10	5	5 996.0	10
3 560.9	9	4	4 172.6	6	1	6 227.7	10
3 598.1	9	2	4 173.2	9	2	6 403.2	8
3 656.9	7	1	4 175.6	7	2	6 576.8	6
3 670.9	7	2	4 200.9§	10	5	6 729.5	9
3 719.5	10	2	4 294.0	8	3	6 806.6	7
3 720.1	10	2	4 311.4	10	3	6 956.0	8
3 752.7p	10	7	4 394.9	8	3	7 060.6	6
3 782.2p	10	4	4 420.5	10	10	7 145.5	8
3 790.1	9	3	4 550.4	6	3	7 148.9	6
3 793.9	10	3	4 616.8	10	2	7 253.52	5
3 836.0	10	2	4 631.8	10	2	7 603.0	6
3 840.3	10	1	4 794.0	10	3			

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Fe 2957.4	*Cd Cr Fe Mn Mo	V 3066.4	
Mo 2891.0		‡Pt 3042.6	‡Mo Na Pt Sr V Zn
V 2908.8		§Fe 4143.9	§Au Bi Co Cr Cu Fe
†Co 3044.0	†Al Au Fe Mo W	Fe 4315.1	Al Au Be Cd Co Cr Fe Mo
Fe 3047.6		Mo 4426.7	Na Ni

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

PALLADIUM

Pd

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
II 2 368.0	1	10	I 3 065.3	4R	4	I 3 894.2	6R	10
2 372.2	2	10	I 3 114.1	5R	8	I 3 958.7	5R	10
2 418.7	1	10	I 3 242.7*	10R	10	I 4 213.0	6R	10
I 2 426.9	1	10	I 3 251.6	5R	6	I 4 473.6	7	4
II 2 433.1	2	10	I 3 258.8	6R	8	I 4 788.2	8	2
2 446.2	1	10	I 3 302.1	6R	10	I 4 817.5	9	2
I 2 447.9	10R	8	I 3 373.0	6R	10	I 5 163.8	10	1
I 2 476.4	10R	2	I 3 404.6P†	10R	10	I 5 295.6	10	2
2 486.5	1	10	I 3 421.2p†	8R	10	I 5 395.3	10
2 488.9p	4	10	I 3 433.4	5R	10	I 5 542.8	10	1
2 498.8p	3	10	I 3 441.4	6R	10	I 5 670.0	10	1
II 2 505.7p	2	10	3 451.4	10	I 5 695.1	9	1
2 551.8	1	10	I 3 460.8	7R	10	I 5 739.7	4
II 2 565.5	1	10	I 3 481.2	7R	10	I 6 130.6	8
II 2 628.2	1	10	I 3 489.8	4R	10	I 6 508.4	6
2 635.9	2	10	I 3 517.0p	8R	10	I 6 774.6	6
2 658.7p	2	10	I 3 553.1	7R	10	I 6 784.6	10	1
I 2 703.1	8R	6	I 3 571.2	5R	10	I 6 833.4	8
2 776.9	10	I 3 609.6p§	9R	10	I 6 916.6	9
2 787.9	10	I 3 634.7p	10R	10	7 194.1	6
2 854.6p	2	10	I 3 690.4	6R	10	I 7 368.1	10
I 2 922.5	7R	3	I 3 718.9	4R	10	I 7 486.9	7
2 980.7	1	10	I 3 799.2	5R	8	I 7 764.0	10
I 3 027.9	4R	6	I 3 832.3	10	10	I 7 915.9	7

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Ti 3239.0	*Cu Mn Ni Sb	§Cd 2288.0	§Ba Cd Co Cu Cr
†Cd 3466.2	†Bi Cd Co Cu Fe	Cr 3593.5	
Co 3453.5		Fe 3618.8	
‡Co 3409.2	‡Ba Co Cr Mo	Fe 3570.1	Au Co Cr Fe Mo
Cr 3408.8		Mo 3614.3	

For explanation of control and interfering line symbols see page 36.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

PHOSPHORUS

P

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 024.0	7	IV 2 739.3	2	III 4 060.4	6
I 2 025.0	6	III 2 884.8	5	III 4 081.2	7
I 2 033.0	6	III 2 896.2	5	4 178.4	5
I 2 034.1	7	V 3 176.1	5	III 4 223.3	7
I 2 136.1	6	III 3 220.2	6	III 4 247.9	7
I 2 136.8p	8	III 3 234.5	6	4 385.3	2
I 2 149.8p	8	IV 3 347.7	6	4 479.7	2
I 2 153.6	6	IV 3 364.4	6	4 587.9	5
I 2 154.8	7	IV 3 371.1	5	4 602.0	5
I 2 534.0	2	4	I 3 424.9	1	3	4 943.4	2
I 2 535.6*L	4	5	3 556.5	2	5 253.5	5
I 2 553.3†	3	5	3 706.1	6	5 296.1	4
I 2 555.0	3	4	3 827.4	3	5 425.9	7
IV 2 725.7	4	3 978.3	6	5 499.7	3

Control lines: Interfering lines:
 *Ag 2660.4 *Ag Co Fe Hg Mn
 Co 2432.2
 Fe 2539.0
 Fe 2538.8

Control lines: Interfering lines:
 †Ag 2480.4 †Ag Cd Co Fe
 Ag 2564.4
 Mn 2551.9

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

PLATINUM

Pt

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 288.2	6	3	2 893.9	6	3	4 498.8	10	10
2 311.0	3	5	2 929.8p§	8R	4	4 520.9	10	4
2 357.1	4R	2	2 998.0p	7R	10	4 522.4	10	10
2 424.9	1	10	3 042.6	4R	4	4 658.0	6	3
2 428.1	8R	2	3 064.7P¶	6R	10	4 684.1	5	1
2 467.4	6R	2	3 139.4	8	3	5 059.5	10	3
2 487.2	4R	2	3 156.6	8	3	5 227.6	10	2
2 628.1	7R	5	3 200.7	7	3	5 301.0	10	5
2 646.9	6R	4	3 204.1	9	4	5 369.0	10	1
2 650.9	4R	4	3 301.9	10	5	5 475.8	10	2
2 659.4p*	10R	10	3 408.14	8	8	5 478.5	10	2
2 702.4†	6R	6	3 485.3	8	3	5 840.1	4	1
2 705.9	5R	5	3 628.1	10	4	6 326.6	10	1
2 719.0	5R	4	3 672.0	8	3	6 523.5	4
2 733.9‡	8R	6	3 923.0	8	10	6 710.4	10
2 771.7	4R	2	4 118.7	10	10	6 842.6	8
2 794.2	5R	6	4 327.1	6	3	7 113.8	10
2 830.3p	8R	5	4 442.6	10	5	7 217.6	6

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Al 3082.2	*Al Cr Ga Mg Mn	In 3258.6	
Cr 2663.4		Mg 2936.5	
Sn 2546.5		Cr 3024.4	Co Cu Cr Mn Mo
†Mn 2610.2	†Ba Co Cr Fe Hg	Fe 2994.4	
Mo 2688.0		Ni 3050.8	
‡Fe 2733.6	‡Cd Fe Mg Mn Mo	¶Co 3044.0	¶Al Bi Co Cu Mo Ni
Mo 2717.3		Fe 3057.5	
§Fe 2957.4	§Ag Cr Fe Mg Mo	Ti 3078.6	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
POTASSIUM

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 078.	10	3 530.7	8	4 466.7	4
2 190.	6	3 608.9	5	4 505.3	5
2 241.	5	3 618.4	5	4 608.4	6
2 550.	5	3 681.5	4	5 005.6	5
3 034.8	4R	3 897.9	8	I 5 099.3	3R	1
3 062.4	5	4 001.2	5	I 5 112.5	3R	1
I 3 102.0	4R	1	I 4 044.2P*F	10R	10R	I 5 323.4	4R	1
I 3 217.2	6R	1	I 4 047.2P†F	10R	10R	I 5 339.9	4R	2
I 3 217.6	4R	1	4 134.7	5	I 5 343.2	4R	1
3 345.7	5	4 149.2	5	I 5 359.7	5R	3
3 363.3	8	4 186.1	10	I 5 782.6	5R	3
3 364.7	6	4 223.0	5	I 5 801.9	6R	4
3 381.1	4	4 225.6	4	I 5 812.4	6R	3
3 385.3	4	4 263.3	8	I 5 832.0	7R	4
3 440.4	3	4 309.0	5	I 6 911.3	10	4
I 3 446.4	8R	3	4 388.1	5	I 6 939.0	10	6
I 3 447.4	6R	2						

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Co 4092.4

*Co Cr Cu Fe Hg Ni Se Ti W

†Co 4092.4

†Co Cr Fe Hg Mn Pt Se Te Ti

Fe 4271.8

Fe 4271.8

Hg 4358.3

Hg 4358.3

Mn 4034.5

Mn 4055.6

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

PRASEODYMIUM

Pr

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 488.8	5	4 223.0	10	10	5 381.3	4	2
2 980.5	8	4 225.3p	10	10	5 469.9	5
2 985.8	8	4 241.0	10	10	5 509.2	4	2
3 687.1	4	3	4 272.3	9	5	5 605.6	5	2
3 739.2	4	3	4 280.1	8	4	5 668.5	6
3 762.4	4	1	4 297.8	8	5	5 707.6	6
3 800.3	5	4	4 305.8	10	10	5 815.2	8	1
3 816.1	9	8	4 334.0	10	8	5 823.7	6	1
3 877.2	10	10	4 368.3	9	8	5 879.2	6	1
3 908.4	10	8	4 405.8	8	5	5 939.9	5	2
3 918.9	7	5	4 408.8	10	10	6 017.8	5	2
3 947.6	9	4	4 429.2	10	10	6 055.1	6
3 964.8	9	4	4 449.8	8	4	6 161.2	5	2
3 972.2	8	3	4 468.7	9	8	6 281.3	5
3 989.7	10	5	4 496.4	10	10	6 359.1	5
3 994.8	10	5	4 510.2	10	10	6 429.7	5	1
4 008.7	10	8	4 517.6	6	2	6 431.9	5
4 054.9	9	6	4 534.2	6	4	6 478.1	5
4 056.5	9	8	4 563.1	5	3	6 566.8	5
4 062.8p	10	8	4 628.7	4	3	6 656.9	6
4 100.8	10	10	4 736.7	4	2	6 673.7	10
4 118.5	10	10	4 783.4	4	1	6 747.2	6
4 141.3	10	6	5 110.4	6	2	6 798.7	8
4 143.1	10	10	5 110.8	6	3	6 827.7	6
4 164.2	10	10	5 173.9	6	4	7 021.6	6
4 179.4p	10	10	5 220.1	5	3	7 114.6	4
4 189.5	10	10	5 322.8	5	3	7 451.7	4
4 206.7	10	10						

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS

RHODIUM

Rh

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 475.6S ₁ G ₁	1	6	3 692.4p [†]	10R	10	5 193.1	10	3
2 490.8	3	10	3 695.5F	7	8	5 354.4	10	5
2 510.7S ₂ G ₂	2	6	3 700.9	10R	10	5 379.1	10	3
2 520.5S ₃ G ₃	2	10	3 748.2	9	10	5 390.4	10	3
2 625.4	2	8	3 765.1	10R	10	5 424.0	10	2
2 705.6	3	10	3 793.2	10R	10	5 535.0	10	1
2 715.3	2	10	3 799.3	10R	10	5 544.6	10	1
2 968.7	5	1	3 822.4	10R	10	5 599.4	10	3
3 263.1	9	2	3 828.5	10R	10	5 686.4	10	1
3 280.5	10R	5	3 833.9	10R	10	5 806.9	10	1
3 283.6	10R	5	3 856.5S ₇ G ₇	10R	10	5 831.6	10	1
3 323.1pF	10R	10	3 934.2	10R	6	5 983.6	8	2
3 396.8p*F	10R	10	3 942.7S ₂ G ₃	10R	6	6 102.7	8	1
3 434.9p [†] F	10R	8	3 958.9S ₃ G ₃	10R	10	6 414.7	8	1
3 462.0	10R	8	4 082.8	10	5	6 519.7	10
3 470.8	10R	8	4 097.5	8	4	6 630.2	10
3 474.8	10R	7	4 128.9	10R	10	6 752.4	10	1
3 478.9	10R	10	4 135.3	10R	10	6 880.0	10
3 502.5 [†]	10R	10	4 211.1F	10R	10	6 965.7	10
3 528.0 [†] F	10R	10	4 288.7	10R	8	7 101.7	10
3 583.1F	10R	8	4 374.8**	10R	10	7 270.8	10
3 596.2FS ₃ G ₄	10R	10	4 379.9	8	3	7 475.7	10
3 597.2S ₆ G ₅	10R	10	4 492.5F	4	3	7 791.6	9
3 626.6	10R	10	4 528.7	10	5	7 824.9	10
3 658.0 S ₇ G ₄	10R	10	4 675.0	10	5	7 830.1	6
3 690.7F	10R	10	4 851.6	10	3			

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Bi 2993.3	*Bi Cu Fe Hg Mo	Mn 3548.0	
Co 3409.2		Mo 3680.7	Co Fe Hg Mn Mo
†Co 3443.6	†Cr Cu Mo Hg Ni	Ti 3234.4	
Ni 3393.0		†Fe 3709.3	*Co Hg Mn Mo Pb
4166.0	‡Ag Ba Co Cr Mo	Mo 3680.7	
Co 3405.1		V 3828.6	
Fe 3558.5		**Cr 4337.6	**Al Bi Cd Co Cr Cu Mo Se Ti
§Co 3506.3	§Au Co Cu Fe Ni	Mo 4377.8	
Fe 3558.5		Mo 4369.1	
Control lines:	Control lines:	Control lines:	
S ₁ Pt 2488.7	3706.5	G ₂ Pt 2513.9	
2482.2	S ₇ Pt 3925.3	2488.7	
S ₂ Pt 2514.0	3923.0	2482.1	
2488.0	S ₃ Pt 3948.4	G ₄ Pt 3638.8	
2482.2	S ₆ Pt 3925.3	G ₅ Pt 3597.2	
S ₅ Pt 2514.0	3923.0	G ₆ Pt 3638.8	
2488.7	G ₁ Pt 2488.7	3706.7	
2482.2	2482.1	G ₇ Pt 3923.0	
S ₄ Pt 3638.8	G ₂ Pt 2513.9	G ₈ Pt 3948.4	
S ₅ Pt 3638.8	2488.7	G ₉ Pt 3923.0	
S ₆ Pt 3638.8	2482.1	3948.4	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

RUBIDIUM

Rb

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 561.9	5	3 662.7	10	4 430.7	10
2 631.8	6	3 699.6	10	4 530.3	6
2 807.6	6	3 801.9	10	4 571.8	10
2 956.1	10	3 940.6	10	4 622.4	10
3 023.7	5	3 978.1	10	4 648.6	10
3 086.9	5	4 083.9	10	4 776.0	9
3 111.4	6	4 104.3	10	4 782.9	7
3 198.8	8	4 136.2	10	4 885.6	5
3 271.0	7	4 193.0	10	5 152.1	6
3 321.5	8	I 4 201.8p*F	10R	9R	5 522.8	6
3 340.6	8	I 4 215.6p†	10R	9R	5 636.0	6
I 3 348.7	4R	4R	4 244.4	10	5 699.2	6
I 3 350.9	5R	5R	4 273.1	10	I 5 724.5	4	2
3 393.1	7	4 293.9	10	I 6 206.5	8	2
3 434.2	8	4 348.3	10	I 6 298.6	10	3
3 461.6	10	4 371.8	10	6 775.1	9
3 492.7	10	4 377.1	10	I 7 280.2	10
3 531.6	10	4 380.7	10	I 7 408.4	10
I 3 587.1	4R	4R	4 401.4	10	I 7 800.3P	10R
I 3 591.6	4R	4R	4 426.1	10	I 7 947.6p	8R
3 600.7	10						

Control lines: Interfering lines:

*Fe 4143.9

*Co Cr Fe Mn Mo Ni Pt Rb

Ru 4297.7

Ru Ti V

Control lines:

†Sr 4077.7

Interfering lines:

†Ag Co Cr Cu Fe Hg Mn Mo

Pd Rh Ru Sc Sr Ti V W

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

RUTHENIUM

Ru

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 402.7L	3	10	I 3 726.9	10R	8	I 5 171.0	10	2
2 456.4L	3	6	I 3 728.0	10R	8	I 5 309.3	10	2
2 661.6L	4	6	I 3 730.4	9R	8	5 361.8	10	1
2 678.7pL	4	10	I 3 742.3	10R	3	5 401.0	10	1
2 692.1p	5	10	I 3 786.0	10R	10	5 427.6	10	1
2 712.4p	4	10	I 3 790.5	10R	10	5 454.8	10	1
2 734.3	4	10	I 3 798.9	10R	10	I 5 484.3	10	1
2 916.3	8	3	I 3 799.3	10R	10	5 510.7	10	1
2 945.7p	3	10	3 923.5	8	5	I 5 636.2	8	3
2 965.6p	3	10	I 4 080.6	10R	10	I 5 815.0	10	1
2 976.6p	4	10	I 4 112.8	9	5	I 5 921.5	10	1
3 177.0	3	8	I 4 199.9	10R	10	I 6 444.8	9
I 3 294.1	8	8	I 4 212.1	10	8	6 690.0	10
3 339.6	8	2	I 4 297.7	10	10	6 824.1	10
3 417.4	10R	3	I 4 372.2	10	10	6 923.2	10
3 428.3	10R	3	I 4 460.0	8	8	6 982.0	10
I 3 436.7p	10R	5	I 4 554.5	10R	10	I 7 027.9	10
I 3 499.0P*	10R	8	I 4 584.5	10	8	7 239.0	9
I 3 593.0	10R	6	I 4 709.5	10	5	7 393.9	8
I 3 596.2p	10R	6	I 4 757.9	10	3	7 499.8	10
3 634.9	10R	3	I 4 815.5	10	3	7 791.9	8
I 3 661.4	8R	10	I 4 869.2	10	3	7 809.2	9
3 726.1F	4R	3	I 5 136.6	10	1	7 881.5	10

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Ba 4166.0

*Cd Cu Fe Mo Rh

Ti 3752.9

Co 3405.1

V 3715.5

Fe 3558.5

†Fe 3795.0

†Cu Fe Hg Mg Mn Rh Sn V W

Rh 3528.0

Fe 3709.3

Rh 3478.9

Rh 3700.9

†Fe 3767.2

†Cd Fe Mn Mn Mo

V 3813.5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

SAMARIUM

Sm

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
3 592.6	5	5	4 544.0	5	5	5 773.8	5
3 634.3	4	4	4 595.3	5	5	5 787.0	5
3 661.4	4	4	4 615.7	5	4	5 814.9	5
3 724.9	6	4 676.9	5	4	5 874.2	4
3 739.2	6	5	4 704.4	5	3	5 938.9	4
3 745.6	5	3	4 760.3	5	2	5 965.7	4
3 986.7	4	2	4 844.2	4	3	6 159.5	4
4 092.3	5	4	4 883.8	4	1	6 256.7	5
4 118.6	6	5	4 910.4	4	1	6 426.6	4	1
4 203.0	6	6	5 044.3	4	1	6 487.7	4	1
4 229.7	6	4	5 071.2	4	1	6 560.3	6	2
4 256.4	5	5	5 271.4	4	1	6 601.8	5
4 280.8L	5	4	5 341.3	5	6 679.3	5
4 281.0L	4	3	5 493.7	6	6 731.9	6
4 319.0	5	8	5 498.2	6	6 794.2	5
4 390.9p	5	10	5 519.6	5	6 861.1	6
4 424.4p	6	10	5 550.4	6R	6 955.3	5
4 434.3pL	6	8	5 626.0	6	7 020.5	5
4 467.3	5	10	5 644.1	6	7 039.2	6
4 519.6	8	5	5 696.7	4	7 082.4	5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
SCANDIUM

Sc

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 062.	4	II 3 581.0	10	10	5 031.0	10	4
2 272.9	4	II 3 589.7	10	10	I 5 081.6	10	2
2 438.6	5	II 3 590.5	10	10	5 239.8	10	2
II 2 552.4	10	10	II 3 613.8p†	10	10	5 349.3	10	1
II 2 560.3	5	6	II 3 630.8p‡	10	10	5 482.0	10	1
2 699.1	6	10	II 3 642.8p	10	10	5 520.5	10	1
2 734.1	4	8	II 3 645.3	10	10	5 526.8	10	3
2 989.0	10	3	II 3 651.8	10	10	II 5 657.9	10	2
I 3 019.3	10	1	I 3 907.5p	10	6	I 5 671.8	10	1
3 039.9	10	2	I 3 911.8p	10	6	I 5 686.9	10	1
3 045.7	10	3	I 3 996.6	10	2	I 5 700.2	10	1
3 052.9	10	4	I 4 020.4	10	8	I 5 711.8	10	1
3 065.1	10	5	I 4 023.7§	10	8	I 6 210.7	10	1
I 3 269.9	5	2	I 4 047.8	7	2	I 6 259.0	10	1
I 3 273.6	5	2	I 4 054.6	8	3	I 6 305.7	10	1
3 353.7	10	10	I 4 082.4	10	3	6 413.4	10
II 3 359.7	10	8	4 165.2	6	6 604.6	4	1
II 3 361.3	10	8	II 4 246.8	10	10	6 737.9	10
II 3 362.0	10	8	II 4 314.1¶	10	10	6 817.1	10
II 3 369.0	10	10	II 4 320.7	10	10	6 819.5	10
II 3 372.2	10	10	II 4 325.0	10	10	6 829.5	10
3 535.7	10	10	II 4 374.5	10	10	6 835.0	10
II 3 558.6	10	10	II 4 400.4	10	10	7 136.1	6
II 3 567.7	10	10	II 4 415.6	10	10	7 697.8	10
II 3 572.6*	10	10	4 670.4	9	10	7 741.2	10
II 3 576.4	10	10	I 4 743.8	10	4	7 800.4	10

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Co 3569.4	*Bi Cr Fe Mn Ni Pb	Mo 3614.3	
Co 3412.3		Mo 3158.2	
Fe 3749.5		§Co 4088.3	§Co Cr Cu Fe Hg Mn Pt Rh
Mn 2949.2		Cu 4062.8	Ru Ti V
Ni 3610.5		Ti 4078.5	
†Cd 2288.0	†Al Au Bi Cd Cr Cs Hg Mg	Pb 4168.0	Co Cr Cu Fe Mn Mo Pt Rh
Mo 3447.1	Mo Ni Rh	Pb 4057.8	Ru Ti V
Ni 3510.3		¶Fe 4282.4	¶A As Au Co Cr Fe Mo Ni
†Fe 3570.1	†Ba Bi Ca Co Fe Mn Sb Sr W	Ti 4335.9	Pd Rh Ru

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
SELENIUM
 Se

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 038.0	2	8	3 387.2	6	4 440.2	2
2 063.7p	8	8	3 514.0	8	4 467.6	3
2 073.0	8	3	3 544.2	10	4 516.2	2
2 354.3	3	3 637.5	10	4 563.9	4
2 459.5	3	3 711.6	6	4 604.3	5
2 591.4	5	3 738.7	10	4 618.7	3
2 630.9	5	3 800.9	8	4 648.4	5
2 685.9	4	3 849.6	2	I 4 730.9P
2 767.4	3	3 877.3	4	I 4 739.1p
2 777.7	3	4 008.1	2	I 4 742.4p
2 837.2	4	4 046.7	2	4 763.6	2
2 880.4	3	4 083.2	3	4 840.5	1
2 914.9	3	4 108.8	3	4 844.8	1
2 951.7	3	4 169.0	3	4 975.7
3 038.7	2	4 176.0	10	4 992.9	1
3 069.9	2	4 182.0	10	5 031.3
3 094.3	3	4 280.3	2	5 068.6	1
3 185.5	3	4 320.4	3	5 096.5	1
3 225.9	3	4 382.8	6	5 142.1	1
3 323.1	3	4 401.0	3	5 176.0	2
3 379.8	3	4 446.0	8	5 227.5	2

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

SILICON

Si

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 124.1	6R	I 2 631.3	5	6	I 3 905.5p	10	5
I 2 216.7	3	3	I 2 881.6p ¶LS ₃	10R	10	IV 4 088.9	6
IV 2 287.1	10	G ₂ N ₂			II 4 128.1	5
I+2 435.159	5R	5	I 2 987.7	5	4	II 4 130.9	6
I+2 506.904p *SiN ₁	10R	6	III 3 590.5	2	III 4 552.7	3
I 2 514.3†N ₂	8R	5	III 3 791.4	6	III 4 567.9	2
I 2 516.1p †LS ₂	10R	10	III 3 796.1	7	III 4 574.8	1
I 2 519.2	8R	5	III 3 806.6	3	II 5 041.1	1
I 2 524.1§G ₁	10R	8	II 3 853.7	3	II 5 056.0	2
I+2 528.516p ¶G ₂	10R	8	II 3 856.0	5	II 5 371.4	2
III 2 541.8	10	II 3 862.6	4			

Control lines: Interfering lines:
 *C₂ 2587.2 *Ag Co Cu Cr Fe V
 †Os 2498.4 †Fe Mn Mo Pt Sb V
 †Pt 2498.5 †Bi Fe Mo Ti V W
 §Co 2519.8 §Bi Fe Mo Ni Pb Pt
 Fe 2541.0
 Fe 2488.2
 ¶Co 2521.4 ¶Au Ba Co Mo Pb Sb
 Co 2564.4

Control lines: Interfering lines:
 Fe 2510.8
 Fe 2522.9
 V 2527.9
 ¶Sb 2598.1 ¶Cd Mg Mo
 Ti 2877.4
 Ti 2884.1
 V 2884.8

Control lines: Control lines: Control lines:
 S₁Cu 2529.4 2997.4 N₁Sn 2495.7
 S₁Cu 2492.2 G₁Fe 2523.6 N₂Sn 2495.7
 2406.7 G₂Fe 2521.7 N₂Sn 2913.5
 S₂Cu 2713.6 G₂Fe 2880.7 2813.6
 2703.3 2926.6 Cu 2882.9
 2882.9

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

SILVER

Ag

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 145.6	1	3	2 460.3	5	3 099.1	2	1
2 162.0	2	2 462.3	4	3 130.0	3	1
2 166.5	2	2	2 473.9	6	3 170.6	2	1
2 186.70	2	3	2 480.4	4	3 180.7	2
2 202.1	2	2	2 504.1	1	3 215.0	2	1
2 229.5S ₁	2	4	2 506.7	2	5	3 223.0	2
2 246.4p	3	3	2 535.3	5	3 233.8	3	2
2 248.7	3	3	2 564.42	6	3 280.7p*FL S ₀		
2 280.0S ₂	1	5	2 575.5	4	1	N ₃ B	10R	9R
2 309.5	6R	4	2 580.7	6	3 305.7	2
2 312.4	4	2	2 595.6	3	3 331.8	2
2 317.0	2	5	2 606.1	6	I 3 382.9p†FL		
2 320.2	2	6	2 614.5	6	S ₇ N ₄	10R	9R
2 321.5	3	2 656.8	6	3 542.5	3	2
2 324.6	2	6	2 660.4	3	5	I 3 682.3	2	1
2 325.1	4	2 681.4	4	I 3 840.8	2	1
2 331.4	4	6	2 688.4	3	I 3 981.6	4	1
2 357.9	6	2 712.1	4	I 3 055.3	8R	3
2 358.9	5	2 721.8	3	2	4 085.9	3
2 362.2	3	2 743.9	3	I 4 212.0	8R	4R
2 364.0	4	2 756.4	6	4 311.1	2	2
2 375.0	4	3	2 767.5	8	4 379.2	2
2 386.3	3	2 786.5	3	4 396.0	2	1
2 390.6	3	2 799.6	6	I 4 476.1	6	4
2 402.6	3	2 815.6	4	4 556.0	3	1
2 411.4	7	2 824.4	6	1	4 615.9	3	1
2 413.2S ₂	4	8	2 873.6	2	4	I 4 668.5	8	3
2 420.1	5	2 896.5	4	4 677.9	2
2 429.7	7	I 2 902.1	4	4 848.1	2
2 437.8pS ₄ N ₁	3	8	2 920.0	3	4 874.2	2	1
2 444.2	4	2 929.3	5	4 888.3	2
2 447.9S ₂ N ₂	2	7	2 934.2	6	I 5 209.0	10R	8
2 453.4	6	2 938.5	4	4			

Control lines: Interfering lines:
 *V 3271.1 *Cu Mn Zn
 Zn 3302.6
 †Mo 3447.1 †Au Cr Sb Sr

Control lines:
 Ni 3393.0
 Sr 3464.5
 Ti 3372.8

Control lines:
 SiSn 2231.7
 S₂Sn 2282.3
 S₂Sn 2408.2
 S₄Sn 2433.5
 Sn 2455.2
 S₂Sn 2433.5
 Sn 2455.2
 S₂Sn 3262.3
 S₂Sn 3218.7
 3330.6
 3650.0

Control lines:
 N₁Sn 2455.3
 2433.5
 N₂Sn 2433.5
 N₃Sn 3223.6
 3218.7
 3141.8
 Pb 3262.3
 3240.2
 3043.9
 N₄Sn 3655.9

Control lines:
 3413.0
 3352.3
 3330.6
 3223.6
 3218.7
 3141.8
 Pb 3240.2
 3230.0
 3220.5
 BMg 2852.1

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
SODIUM

Na

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 490.7	1R	2 980.	4	I 4 665.0	3	3
2 493.3	2	2 984.3	4	I 4 669.0	4	3
I 2 512.1	1R	1	3 056.3	3	I 4 748.1	3	2
I 2 512.2	1R	1	3 078.5	4	I 4 752.0	4	2
I 2 543.8	2R	1	3 093.0	6	I 4 979.0	5	4
I 2 543.9	1R	1	3 129.0	6	I 4 983.2	6	4
I 2 593.8	3R	3	3 189.0	4	I 5 675.8	8
I 2 593.9	2R	3	3 285.0	5	I 5 682.8	8	8
I 2 680.3	4R	4	I 3 302.3p*	9R	9R	I 5 688.3	10	8
I 2 680.4	3R	4	I 3 302.9p	8R	8R	I 5 890.0F ^b	10R	8
2 847.0	4	3 533.1	8	I 5 895.9pF	8R	10
I 2 852.8	5R	5	3 631.0	5	I 6 154.4	4	3
I 2 853.0	4R	5	3 711.0	3	I 6 160.8	5	4
2 951.4	5	I 4 393.0	3	1	I 6 183.3	8

Control lines: Interfering lines:
*Fe 3407.5 *Cr Pt Sr Ti Zn

Control lines:
Zn 3345.0

STRONTIUM

Sr

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 428.1	3R	I 4 811.9	6R	4	I 5 543.3	5	2
I 2 569.5	3R	I 4 832.1p	6	3	I 5 598.4	6	1
I 3 301.7	5	2	I 4 855.1	4	1	I 6 364.0	4	1
I 3 307.5	4	1	I 4 872.5p	6	2	I 6 370.0	4	1
I 3 322.2	5	1	I 4 876.1	6	1	I 6 380.7	5	1
3 330.0	4	2	I 4 876.3	6	1	I 6 386.5	7	1
I 3 351.3	6R	2	I 4 892.0	6	2	I 6 388.3	6	1
II 3 366.3	5	2	I 4 962.3P	6R	2	6 408.5	9	4
II 3 380.7	5	6	I 4 967.9	4	1	6 504.0	8	4
I 3 464.5	6	7	I 5 156.1	5	1	6 546.3	5	2
I 3 940.8	5	2	5 222.2	5	1	6 550.3	6	3
II 4 030.4	5	4	5 225.1	5	1	6 617.3	6	3
II 4 077.7p*	10R	10R	5 229.3	5	1	6 643.6	5	2
II 4 161.8	4	3	5 238.6	6	1	I 6 791.1	6	1
II 4 215.5p†	9R	9R	5 256.9	6	3	I 6 878.4	10
I 4 305.5	4	4	I 5 480.9	7	4	I 7 070.2	10R	1
I 4 361.7	4	2	I 5 486.1	5	2	I 7 167.3	6
I 4 438.0	6	3	I 5 504.2	5	3	I 7 232.2	5
I 4 607.3p†F	10R	6R	I 5 521.8	6	3	I 7 309.5	7
I 4 722.3	6	3	I 5 534.8	5	2	I 7 621.5	5
I 4 741.9	5	1	I 5 540.0	5	2	7 673.1	6

Control lines: Interfering lines:
*Mn 4055.6 *Au Bi Co Cr Fe Hg Mn Mo
Cb 4059.0 Se Ti W
Ti 4295.8

Control lines: Interfering lines:
†Rb 4201.8 †Ag Co Cr Cu Fe Hg Mn
‡Fe 4619.3 †Al Au Be Co Cr Cs Fe Li
Mo 4626.5 Mn Mo Pt Se Ti V W

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

SULFUR

S

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
3 098.4	5	4 694.2p	10	5 579.1	6
3 497.3	8	4 695.5p	8	5 606.1	8
3 717.7	5	6	4 696.3p	6	5 614.3	5
3 837.4	4	7	4 925.3	6	5 640.0	8
3 838.3	8	8	5 009.6	6	5 647.1	8
3 928.5	8	5 014.0	8	5 660.1	6
3 983.7	5	5 032.5	8	I 5 696.8	6
3 993.5	5	5 201.0	6	I 5 700.4	7
4 028.8	6	5 212.6	1	8	I 5 706.2	8
4 142.5	2	8	5 278.1	3	I 6 042.0	5
4 145.1	2	10	5 278.6	5	I 6 046.0	6
4 253.2	10	5 279.0	6	I 6 052.8	7
4 163.	3	10	5 320.7	8	6 538.1	6
4 174.3	1	7	5 345.7	8	I 6 743.7	5
4 189.9	5	5 428.7	9	I 6 748.8	6
4 253.6	8	5 432.8	10	I 6 757.2	7
4 285.0	5	8	5 453.8	10	7 244.8	6
4 294.4	8	5 473.6	8	7 679.6	4
4 332.7	1	5	I 5 507.0	5	7 686.1	6
4 362.5	6	5 509.6	10	7 696.7	8
4 525.0	6	5 564.9	8			

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

TANTALUM

Ta

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 035.6*	4	3	3 436.0	5	1	5 136.5	3	3
2 047.5†	3	2	3 497.9	5	5 461.3	4	2
2 653.3‡	3	2	3 511.0	8	2	5 518.9	3	2
2 675.9§	3	5	3 566.7	4	1	5 664.9	6	3
2 685.1	3	5	3 607.4	7	2	5 776.7	7	2
2 714.7¶	3	2	3 626.6	9	3	5 811.1	8
2 758.3	3	1	3 642.1	10	2	5 822.3	5
2 802.1	3	1	3 918.5	3	2	5 997.2	7
2 891.9	4	1	4 027.0	4	2	6 045.4	5
2 933.6	5	2	4 067.9	6	2	6 258.6	8	2
2 965.2	4	4	4 129.4	5	2	6 268.7	8	2
3 012.5	5	3	4 175.2	4	3	6 309.6	8	3
3 049.5	5	1	4 205.9	6	2	6 389.4	8	3
3 103.3	5	1	4 279.1	3	2	6 430.8	9	5
3 125.0	4	1	4 415.7	3	3	6 450.4	10	5
3 170.3	4	1	4 511.0	8	3	6 485.4	10	10
3 223.8	4	2	4 530.8	5	3	6 514.4	9	3
3 242.1	4	4 574.3	5	3	6 516.1	10	3
3 311.1P	9	3	4 681.9	5	5	6 673.7	4	1
3 317.9	7	1	4 740.1	4	2	6 675.5	5	2
3 361.6	5	1	4 812.7	4	2	6 866.2	3	1
3 406.9p	5	2	4 936.4	3	1			

Control lines: Interfering lines

*Fe 2692.6 *Ba Cr Fe Mn Mo Te V W
Mo 2688.0
†Be 2348.6 †Ba Fe Pb
Mo 2644.3
‡Al 2660.3 ‡Al Hg Mo Pb Sb W
§Cr 2835.6 §Au Co Sb V W

Control lines: Interfering lines:

Pt 2650.9
V 2677.8
||Cr 2691.1 ||Co Cr Fe Mo Ti
Mo 2775.4
¶Fe 2727.5 ¶Be Fe In Mn Pt
Mo 2701.4

TELLURIUM

Te

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 081.8	S	2 265.5	5R	3	5 045.2	4
2 143.0p	9R	1	2 283.3p*	10R	10R	5 449.7	5
2 147.3	S	1	2 385.8p†	10R	10R	5 649.3	10
2 160.1	6	1	2 530.7p	7	5	5 708.1	10
2 208.9	6	2	2 769.7p	9	4	5 755.8	8
2 255.5	5R	3	3 175.1	9	2	6 438.0	10
2 259.0	8R	3	4 866.5	4			

Control lines: Interfering lines:

*Co 2378.6 *Ag Co Cr Fe Ir Mn
Fe 2380.8

Control lines:

†Au 2352.7
Co 2383.5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
TERBIUM
Tb

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 658.9	10	3 981.9L	10	10	4 837.6	6	1
2 891.3	10	4 005.6	8	10	4 875.6	6	1
2 909.2	10	4 012.9	7	5	4 881.1	6	2
2 913.3	10	4 033.1	8	8	4 915.9	6
3 078.9	4	8	4 066.2	5	3	4 931.8	6
3 293.1	5	8	4 094.4L	5	4	4 971.0	5
3 324.4	8	5	4 144.5	5	10	4 993.9	6
3 413.8	5	4	4 187.2	5	5 065.8	5
3 454.1	7	4	4 235.4L	5	4	5 089.1	5	1
3 509.1p	10	10	4 278.5	10	10	5 228.1	5
3 561.8p	10	10	4 318.9	6	3	5 319.2	5
3 568.5	7	5	4 342.5	6	2	5 369.7	5
3 628.2	8	3	4 353.2	6	3	5 376.0	5
3 638.5	7	5	4 356.8	6	2	5 424.1	5
3 650.4	7	8	4 367.3	5	3	5 470.3	5
3 658.9	8	8	4 423.1	5	1	5 524.1	5
3 676.0	8	10	4 493.1	5	2	5 685.7	5
3 702.9	6	10	4 511.5	6	5 747.6	6
3 703.9	8	8	4 563.7	6	1	5 785.2	5
3 711.8	10	4	4 578.7	8	3	5 803.1	5
3 765.1	6	8	4 642.0	8	3	5 851.1	5
3 776.5	8	8	4 645.3	9	2	5 967.4	5
3 848.8p	10	10	4 662.8	6	1	6 039.0	4
3 874.2p	10	10	4 681.9	8	6 331.7	4
3 899.2	8	8	4 702.4	8	2	6 677.9	6
3 925.5	10	10	4 734.2	6	1	6 785.1	4
3 939.5	10	10	4 739.9	6	1	6 794.6	5
3 976.9	10	10	4 752.5	10	8	6 896.4	5

THALLIUM
Tl

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 2 237.8	6R	3R	I 2 710.7	4R	4	I 3 529.4	8R	10
I 2 316.0	6R	4	I 2 767.9S ₄	10R	10	I 3 775.7p†LS ₁₀	10R	10R
I 2 379.6S ₁	8R	10R	I 2 826.2S ₄	8R	4 738.1	10
I 2 552.5	6R	I 2 918.3S ₇	10R	1	I 5 350.5P†	10R	10
I 2 580.2S ₂	8R	6R	I 2 921.5	6R	1	5 948.9	8	8
2 665.6S ₁	4	4	I 3 229.8S ₄	10R	1	I 6 550.0	8	3
I 2 709.2S ₄	8R	6R	I 3 519.2*LS ₉	10R	10R	6 714.0	5	2

Control lines:	Interfering lines:	Control lines:	Control lines:
*Co 3409.2	*Co Cr Cu Fe Mn	S ₁ Pb 2393.8	S ₇ Pb 2926.8
Fe 3558.5		S ₂ Pb 2577.3	S ₈ Pb 3240.2
V 3558.8		S ₃ Pb 2657.2	2657.2
†Ti 3786.0	†Fe Mo Ni Sb Ti	S ₄ Pb 2697.5	S ₉ Pb 3220.5
V 3750.9		S ₅ Pb 2657.2	3262.4
†Fe 5307.4	†Al Ba Be Ca Co Cr	S ₆ Pb 2657.2	S ₁₀ Pb 3740.0
			4019.6

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
THORIUM

Th

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 413.5	6	4 069.2	3	7	5 539.9	5	2
2 428.0	8	4 085.1	3	7	5 604.5	4	1
2 431.7	7	4 116.8	2	6	5 639.7	5	1
2 441.3	9	4 178.0	3	5	5 707.1	4	1
2 463.7	7	4 208.9	4	8	5 749.3	4	1
2 512.7	8	4 381.9§	5	10	5 815.4	4
2 686.2	6	4 391.1	5	10	5 870.5	4	1
2 837.3*	4	5	4 510.5	4	5	5 914.4	4	1
2 898.9	6	4 602.9	5	1	5 989.0	7	2
2 978.7	8	4 619.5	7	3	6 015.4	4	1
3 097.9	6	4 740.5	6	4	6 087.3	5	1
3 108.3	4	5	4 752.4	6	4	6 099.6	4	1
3 188.2	5	5	4 761.1	5	3	6 104.8	4	1
3 216.6	8	4 774.3	5	2	6 112.8	4	1
3 221.3	2	10	4 818.6	4	4	6 120.6	4	1
3 232.1	1	7	4 832.8	5	2	6 261.1	4	1
3 290.6p	10	4 863.2	9	8	6 274.1	4	1
3 300.5	1	10	4 919.8	9	6	6 342.9	4
3 313.7	1	10	4 934.2	5	1	6 358.6	4
3 392.1	4	5	4 987.2	5	3	6 376.9	4
3 469.9	4	5	5 017.2	8	3	6 396.4	4
3 507.6	10	5 028.6	5	2	6 411.9	4
3 511.6	5	6	5 049.8	7	3	6 416.1	4
3 538.8p	1	10	5 068.0	5	6 457.3	4
3 601.1p	3	7	5 148.2	4	2	6 462.6	5	1
3 617.1	4	5	5 247.7	5	2	6 531.3	4
3 659.1	3	6	5 277.5	5	2	6 584.0	4
3 741.2 †	5	6	5 325.1	4	2	6 989.7	4
3 752.6	4	6	5 435.9	4	1	6 993.1	4
4 019.1p‡	5	10	5 462.6	4	1	7 054.8	4

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Cr 3605.3

*Al Au Cd Cu Fe Mn Pt Sb

Mn 4048.8

§Al Bi Co Cr Fe Ga Mo Ni Pb

Sn 2863.3

Sn W

§Cr 4371.3

†Fe 3749.5

†Cu Fe Mn Mo Pb Ti

Fe 4045.8

Fe 3787.9

Mo 4277.3

Pb 3572.7

||Pb 4245.2

||Al Bi Co

Ti 3752.9

Ti 4427.1

‡Co 4086.3

‡Co Cr Fe Mn Mo Ni Ti V W

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

TIN

Sn

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 039.5	4R	2 495.7	5R	4R	3 262.3p§LP ₄	10R	5R
2 072.9	5R	2 546.6S ₂₂ N ₃	5R	5R	3 283.5	10
2 096.3	4R	2 571.6S ₁₂ G ₃ N ₃	5R	5R	3 330.6S ₁₀ N ₁₃	6R	6
2 100.8	4R	2 594.4S ₁	4R	3R	3 352.3	10
2 113.9	4R	1R	2 637.0S ₂	3 655.9S ₄
2 121.2	3R	2 658.6	10	3 801.0S ₇ N ₉	9R	8R
2 140.6	3R	1	2 661.3S ₂	5R	4R	4 524.7pN ₁₀	6	10
2 151.4	3R	2	2 706.5S ₉ N ₇	7R	7R	4 585.6	10
2 194.5	3R	2R	2 761.8S ₃ G ₄	5 332.7	10
2 199.3	3R	2R	2 765.0S ₂₈	5 562.7	10
2 209.6S ₂₂ N ₁	3R	2R	2 779.8	4R	5	5 589.4	10
2 231.7	4R	2	2 785.0	3R	4	5 731.7	7	3
2 246.1	3R	3R	2 813.6	5R	4R	5 799.4	10
2 268.9	3R	3R	2 840.0*LS ₂ N ₃	8R	10R	5 970.3	5
2 282.3S ₂₀	3R	2 850.6S ₄ B ₁	6R	7R	6 037.7	5
2 286.7	4R	3R	2 863.3p†S ₂₂ N ₃ B ₂	8R	8R	6 054.9	5
2 317.2	5R	4R	2 913.5	6R	4	6 069.0	7
2 334.8S ₁₄	4R	4R	3 009.1pS ₁₁ N ₁₀ B ₃	9R	8R	6 149.6	6
2 364.8S ₂₂ G ₁ N ₂	5R	6R	3 032.8	3R	3	6 154.6	5
2 380.7S ₁₈	3R	2	3 034.1p†S ₁₁ N ₁₁	9R	8R	6 171.5	4
2 408.2	4R	3	3 141.8S ₁₇	4	4	6 310.8	4
2 421.7S ₁₃ G ₂ N ₃	6R	8R	3 175.1pLS ₁₀ N ₁₂	10R	9R	6 453.5	3	6
2 429.5N ₄	7R	8R	3 218.7S ₁₈	3	3	6 579.2	4
2 483.4	5R	4R	3 223.7S ₁₉			

Control lines:

Interfering lines:

*Cr 2835.6

*Al Cr Fe Mn Mo Pb

Ti 3202.5

†Fe 2863.9

As 2780.2

Cr 2849.8

Cr 2865.1

†Bi Fe Mn Mo Sb

Control lines:

W 2896.4

†Fe 3047.6

V 3188.5

V 3187.7

§Fe 3268.2

Cd 2288.0

Interfering lines:

†As Au Bi Co Cr K

§Ra Cd Fe Mo Pb

Control lines:

S₁Pb 2614.2

2562.4

S₂Pb 2614.2

Bi 2627.9

S₃Pb 2663.2S₄Pb 2823.2

2873.3

2802.0

Bi 2696.8

S₅Pb 2833.1

2802.0

2938.3

2898.0

S₆Pb 4057.8

Cd 3404.7

3467.7

Control lines:

3466.2

3610.5

3614.4

S₇Pb 4057.8S₈Pb 2657.2S₉Pb 2717.2

2628.3

S₁₀Pb 3176.5

Bi 3067.7

S₁₁Pb 3043.9

3036.1

S₁₂Pb 2657.2

2628.3

2562.4

S₁₃Pb 2411.8

2388.8

Control lines:

2399.6

Cu 2406.7

S₁₄Pb 2332.5S₁₅Pb 2399.6S₁₆Cd 3403.7S₁₇Cd 3403.7

Bi 2938.3

3067.7

3024.6

S₁₈Cd 3403.7

3466.2

3467.7

Bi 3019

3067.7

S₁₉Cd 3403.7

3466.2

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS

TIN (Continued)

Control lines:

SnCd	3467.7
Bi	3067.7
SnCd	2288.0
SnBi	3067.7
Bi	2898.0
Cu	2938.3
SnPb	2218.1
SnPb	2562.4
SnCu	2858.3
	2882.8
Bi	2938.3
SnCu	2356.5
SnBi	2730.5
	2938.3
G1Pb	2389
G2Pb	2412
G3Pb	2629

Control lines:

G1Pb	2629
	2657
NiPb	2218.1
NsSn	2317.2
Pb	2399.6
	2388.6
NsSn	2880.7
Pb	2411.9
	2399.6
NsSn	2380.7
NiPb	2562.4
NiPb	2657.2
N7Pb	2657.2
	2628.3
NsSn	2850.6
NsSn	2913.5
	2850.6

Control lines:

Cu	2913.5
N10Sn	2913.5
Pb	3043.9
	2973.0
N11Sn	2913.5
Pb	3119.2
N12Pb	3119.2
N13Pb	3119.2
N14Pb	3786.2
N15Pb	5042.7
B1Pb	2802.0
B2Cu	2766.4
Pb	2873.3
B3Cu	2961.2
B4Cu	2766.4
Cu	3274.0
Fe	3268.3

TITANIUM

Ti

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
III 2 346.8	6	I 2 948.3	9	2	II 3 349.0P	6R	8R
III 2 375.0	6	I 2 956.1	10	2	II 3 349.4†	9R	10R
I 2 384.5	3	1	I 2 967.2	8	2	I 3 354.6	8	3
2 414.0	10	III 2 984.8	10	II 3 361.2p†	8R	10R
I 2 418.4	3	1	II 3 072.1	8	3	I 3 370.4	9R	2
III 2 516.0	10	II 3 073.0	8	3	I 3 371.5	9R	2
II 2 525.6	4	10	II 3 075.2	9	4	II 3 372.8L	10	10R
III 2 527.8	10	II 3 078.7	9	6	II 3 380.3	7	10
III 2 540.0	10	II 3 088.0	10	10R	II 3 383.8B1	8R	10
III 2 563.4	10	II 3 162.6	9	6	I 3 385.0	8R
I 2 599.9	6	2	II 3 168.5	9	10	II 3 387.8	8	10
I 2 611.3	7R	1	I 3 186.5	9R	3	II 3 394.6	2	10
I 2 619.9	5	1	II 3 190.9	7	10	II 3 444.3	4	10
I 2 641.1	9	2	I 3 192.0	9R	1	II 3 452.5	1	8
I 2 644.3	9	3	I 3 199.9	9R	3	II 3 456.4	2	9
I 2 646.6	9	2	II 3 202.5	6	10	II 3 461.5	9	10
I 2 662.0	5	II 3 217.1	8	8	II 3 477.2	9	10
I 2 669.6	6	2	II 3 222.8	7	8	II 3 504.8	7	10
I 2 742.3	7	4	II 3 224.2	5	8	II 3 510.9	8	10
II 2 751.7	8	II 3 234.5*	8R	10R	II 3 520.3	3	8
I 2 758.1	6	1	II 3 239.0	7R	6R	II 3 535.5	4	10
II 2 805.0	10	II 3 242.0	7	10	I 3 635.5p	9R	3
II 2 810.3	4	10	II 3 248.6	4	10	II 3 641.3	4	10
II 2 817.8	10	II 3 261.6	4R	10	I 3 642.7p	10R	3
II 2 828.1	3	8	II 3 322.9	8R	10	I 3 653.5p	10R	4
II 2 841.9	8	4	II 3 329.5	6	10	II 3 659.8	4	10
II 2 884.1	7	8	II 3 332.1	5	8	II 3 662.2	4	10
I 2 912.1	8	2	II 3 335.2	7	10	II 3 685.2	10R	10
I 2 942.0	9	4	I 3 341.9	6R	10R	II 3 706.2	2	8

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
 PRINCIPAL LINES BY ELEMENTS
 TITANIUM (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 3 729.8	SR	4	I 4 518.0	9	4	I 5 210.4	SR	9
I 3 741.1	10	2	I 4 522.8	9	4	II 5 226.6	3	10
I 3 741.7	3	10	I 4 527.3	10	4	I 5 283.5	7	3
I 3 752.0	10	5	I 4 533.3*	10R	5	I 5 297.3	7	3
II 3 759.3L	9	10	I 4 534.8**	9R	4	II 5 336.8	3	10
II 3 761.3L	8	10	I 4 535.6††	SR	3	I 5 477.7	9	4
I 3 882.9	9	3	I 4 535.9‡‡	6R	I 5 488.2	6	3
II 3 900.5	5	10	I 4 536.1§§	6R	4	I 5 512.5	8	10
II 3 913.5	5	10	I 4 544.7	9	3	I 5 514.4	7	8
I 3 947.8	8	3	I 4 548.8	9	3	I 5 514.5	8	8
I 3 948.7	10	4	II 4 549.6	5	10	I 5 565.5	7	8
I 3 956.3	10	4	I 4 555.5	9	3	I 5 644.1	7	10
I 3 958.2	10	5	II 4 563.8	4	10	I 5 662.2	7	8
I 3 962.9	7	3	II 4 572.0	6	10	I 5 662.9	7	3
I 3 964.3	7	3	I 4 623.1	9	3	I 5 675.4	7	4
I 3 989.8	10	6	I 4 656.5	8	3	I 5 689.5	8	3
I 3 998.6§	10	6	I 4 667.6	10	5	I 5 702.7	6	2
I 4 009.7	7	4	I 4 681.9	9	6	I 5 708.2	5	1
I 4 024.6	7	3	I 4 691.3	8	4	I 5 715.1	8	2
I 4 078.5	6	4	I 4 698.8	8	3	I 5 762.3	7	2
II 4 163.7	4	10	I 4 731.2	5R	3	I 5 766.3	7	3
II 4 171.9	3	10	I 4 758.1	8	5	I 5 806.4	9	10
I 4 274.6	10	4	I 4 759.3	8	6	I 5 899.3	9	10
I 4 282.7	6	3	I 4 820.4	7	3	I 5 918.5	6	3
I 4 287.4	9	4	I 4 840.9	9	4	I 5 922.1	7	4
I 4 289.1	10	4	I 4 870.1	7	3	I 5 941.8	7	4
II 4 290.2	4	10	I 4 885.1	8	5	I 5 953.2	8	10
I 4 290.9	8	2	I 4 981.7p	9	10	I 5 965.8	8	10
II 4 294.1	6	10	I 4 991.1p	9	10	I 5 978.5	8	8
I 4 298.7	10	4	I 4 999.5p	10	10	I 5 999.7	6	2
II 4 300.1	6	8	I 5 007.2p	9	10	I 6 085.2	7	4
I 4 300.6	10	2	I 5 014.3	10	9	I 6 091.2	7	5
I 4 301.1	10	3	I 5 020.0	8	5	I 6 126.2	9	5
I 4 305.9	10	8	I 5 022.9	9	5	I 6 215.3	7	10
II 4 307.9	8	I 5 024.9	9	3	I 6 258.1	9	9
I 4 314.8	7	3	I 5 025.6	8	3	I 6 258.7	9	9
II 4 337.9	5	10	I 5 035.9	7	9	I 6 261.1	9	9
II 4 395.0	7	10	I 5 036.5	9	8	I 6 303.8	6	3
I 4 427.1	8	4	I 5 038.4	9	8	I 6 556.1	6	5
I 4 443.8	6	10	I 5 040.0	9	3	I 6 743.2	5	3
II 4 455.3	10	4	I 5 064.7	10	5	I 6 861.2	5	1
I 4 457.4	9	5	I 5 173.7	7R	7	I 7 209.5	8
I 4 468.5	6	10	II 5 188.7	4	10	I 7 244.9	5
II 4 501.3	5	10	I 5 193.0	SR	10	I 7 251.7	6
I 4 512.7	10	4						

Control lines: Interfering lines:

*Ni 3057.6 *Cr Cu Fe Mn Mo Ni

†Mn 3350.4 †Ca Co Cu Mn Mo Sc Sr

‡Mo 3447.1 ‡Ca Co Cr Mo Ni Sc Te

§Co 4092.4 §Co Fe Ga Mn Mo

**Ca 4318.6 **Ba Bi Ca Cd Co Cr Fe

Control lines: Interfering lines:

††Co 4092.4 ††Al Be Co Cr Cu Fe

Cr 4526.5

‡‡Cr 4526.5 ‡‡Al Be Co Cr Mn Mo

§§Cr 4526.5 §§Al Be Cr Cu Mn Mo

B:Cr 3368.1

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

TUNGSTEN

W

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 397.1p	2	10	3 049.7	6R	1	5 071.7	5	10
2 446.4	1	8	3 077.5	1	10	5 224.7	10	10
2 488.8	2	6	3 376.1	1	10	5 492.3	10	10
2 571.5	2	6	3 401.9	1	8	5 514.7	10	10
2 572.3	6	3 508.7	6	5	5 648.4	7	10
2 579.3	1	5	3 545.2	6	3	5 735.1	8	8
2 579.6	7	3 572.5	3	10	5 804.9	7	5
2 589.1pB ₁	2	8	3 592.4	3	10	5 947.6	4	2
2 658.0	2	8	3 613.8p	3	10	6 012.8	4	3
2 702.1	1	10	3 617.5	8R	2	6 292.1	4	2
2 762.3	4R	2	3 641.4	4	10	6 404.2	4	2
2 764.3	4R	8	3 736.2	1	10	6 445.2	4	2
2 769.0	4R	1	3 808.0	5	5	6 538.2	4
2 769.8	4R	1	4 008.8P†	10	10	6 693.1	5
2 770.9	4R	1	4 074.4§	7	6	6 820.7	4
2 774.0	5R	2	4 215.4	3	8	6 934.3	4
2 774.5	5R	3	4 294.6p	6R	9	6 984.3	4
2 818.1	5R	2	4 302.1p¶	8	5	7 140.5	3
2 879.1	5R	2	4 484.2	8	4	7 296.6	3
2 879.4	5R	2	4 570.7	7	3	7 385.1	3
2 896.0	4R	2	4 588.7	7	3	7 483.4	3
2 935.0	5R	3	4 680.5	8	5	7 569.9	3
2 944.4*	7R	3	4 843.8	9	5	7 614.1	3
2 947.0†	8R	3	5 006.2	8	10	7 688.9	3
3 017.4	6R	2	5 015.3	8	8	7 784.1	3
3 041.9	5R	1	5 053.3	10	2	7 940.9	3
3 046.4	5R	1						

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Fe 2912.2

*Ba Co Fe Ga Mn Mo

||Fe 4132.1

||Al Cr Fe Mn Mo Ni

Ga 4033.0

Mo 4292.1

Ti 2956.1

Ti 4298.7

†Fe 2936.9

†Cr Hg Mo

V 4291.8

Cb 3225.5

4226.7

*Bi Ca Co Cr Fe

Mn 2605.7

Fe 4132.1

‡Ti 4024.6

‡Co Fe Mn Mo Ni

BiMn 2593.7

4063.6

§Cr Cu Fe Mn Mo

For explanation of control and interfering line symbols see page 1

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

URANIUM

U

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 008.0	5	4 731.6	5	3	5 915.4	8	1
3 566.6	4	2	4 756.8	5	2	5 976.3	5
3 670.1*	4	3	4 772.7	4	3	5 997.3	4
3 831.5	4	3	4 819.5	4	2	6 051.7	4	1
3 859.6†	5	3	4 899.3	4	2	6 077.3	4
3 932.0	5	3	5 027.4	5	4	6 171.9	4
3 985.8	5	2	5 280.4	4	1	6 372.5	5
4 090.1‡	6	4	5 475.7	5	3	6 395.5	6
4 156.7	5	2	5 481.2	5	3	6 449.2	10	1'
4 163.7	5	2	5 492.9	8	4	6 465.0	4
4 171.6	5	3	5 527.8	10	4	6 826.9	4
4 241.7p§	5	4	5 564.2	5	1	7 074.8	4
4 287.9	4	3	5 610.9	5	1	7 128.9	4
4 341.7	5	4	5 621.5	4	1	7 425.5	3
4 393.6	5	2	5 669.5	4	7 533.9	5
4 472.3	5	6	5 723.6	5	1	7 631.7	3
4 543.6	5	8	5 758.2	6	7 784.1	5
4 627.1	5	5	5 780.6	4	7 881.9	4
4 646.6	4	4	5 798.5	4	1	7 970.4	3
4 689.1	5	4	5 837.7	4	1			

Control lines: Interfering lines:
 *Ti 3771.7 *Co Fe Hg Li Mn
 †Fe 4071.7 †Ba Cr Cu Fe
 Fe 3820.4
 Mo 3798.3
 Ni 3510.3

Control lines: Interfering lines:
 ‡Fe 4088.6 ‡Au Bi Co Cr Fe
 Co 4118.8
 V 4099.8
 §Pb 4168.0 §As Au Ba Ca Co Cr Mg
 Pb 4057.8 Mn Mo Pb

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

VANADIUM

V

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 074.5	15	II 3 118.4p	10R	10R	3 787.2	2	8
2 677.8	7	4	II 3 125.3p	8	2	3 795.0	8	3
2 678.6	7	3	II 3 126.2	6	4R	I 3 813.5	8	3
2 679.4	8	4	II 3 130.3B ₂	5	10R	3 815.5	3	10
2 688.0	10	5R	3 134.9	2	8	I 3 818.2	8	3
2 701.0	8	5R	3 136.5	2	8	3 847.3	4	10
2 706.2	8	3R	3 139.7	1	8	I 3 855.9	9R	3
2 715.7	10	5	I 3 183.4p	10R	2R	I 3 864.9	8	3
2 810.2	2	8	I 3 184.0P†	10R	2R	I 3 875.1	SR	2
2 882.5	6	8	I 3 185.4p‡	10R	2R	3 878.7	1	10
2 884.8	6	10	3 187.7	5	8R	3 902.3	SR	2
2 891.7L	10	6R	3 188.5	5	8R	I 3 909.9	6R
2 892.5	10	3 190.7	7	10R	3 914.3	2	8
2 892.7	10	5R	3 198.1	5R	2	3 918.4	2	8
2 893.3	10	5R	I 3 202.4	5R	2	3 952.0	3	10
2 904.1	8	1	3 217.1	6	10	3 973.6	3	10
2 906.1	8	4R	3 237.9	6	10	3 990.6	10	6
II 2 907.5	8	3R	3 254.8	2	8	3 997.1	3	8
2 908.8	8R	8R	3 267.7	10	10R	3 998.7	8	4
2 910.0	8	4R	3 271.1	10	10R	4 005.7	3	10
2 910.4	8	4R	3 276.1	10	10R	4 023.4	2	10
II 2 911.1	6	3R	3 279.8	3	10	4 035.6	2	10
2 914.9	10	2	3 337.9	8	I 4 090.6	10	10
2 920.0	8	2	3 457.1	2	10	I 4 092.7	10	3
II 2 920.4	8	3	3 496.9	3	8	I 4 099.8	10	2
2 923.6	8R	3 504.4	4	10	I 4 105.2	10	4
II 2 924.0L	8	8R	3 517.3	5	10	4 111.8]	10R	2
II 2 924.7	8	8R	3 524.7	3	8	I 4 115.2	10	2
II 2 930.8	8	5R	3 530.8	6	10	I 4 116.5	8	7
II 2 941.4	3	10R	3 545.2	6	10	I 4 116.7	10R	7
2 942.4	10R	2	3 556.8	4	10	I 4 128.1	10	10
2 943.2	8	1	3 566.2	3	8	I 4 132.0	10R	10
II 2 944.6	2	8R	3 589.8	5	10	I 4 134.5	9	10
II 2 952.1	8	8R	3 592.0	5	10	4 183.4	2	10
2 955.8	8	3 593.3	5	10	4 202.4	1	8
II 2 957.5	8	6	3 619.0	1	8	4 205.1	2	10
2 968.4	8	10R	3 667.7	8	3	I 4 209.9	6	8
2 974.2	8	1	3 669.4	1	8	4 268.6	8	8
2 976.2	8	2	I 3 688.1	8	3	4 271.6	6	8
2 977.6	8	1	I 3 690.3	8	4	4 277.0	6	8
3 001.2	3	8R	I 3 692.2	8	4	4 284.1	7	10
3 044.9	4R	1	3 695.9	8	3	I 4 330.0	6	10
3 050.9	3R	3	3 700.3	1	8	I 4 332.8	8	10
3 056.4	3R	2	I 3 703.6	8	3	I 4 341.0	9	10
3 060.5	3R	3 715.5	6	10	I 4 352.9	10	6
3 066.4	4R	1R	3 727.5	10	I 4 379.2†	10R	10R
II 3 093.1P*LB ₁	4	10R	3 732.8	5	10	I 4 384.7**	10R	10R
II 3 102.3p†	10	10R	3 745.8	3	10	I 4 390.0††	10R	10R
II 3 110.7p	8	10R	3 771.0	3	10	I 4 395.2	10	10

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
VANADIUM (Continued)

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
I 4 400.6	9	10	I 4 619.7	8	9	I 6 039.7	10	10
I 4 406.7	8R	5R	I 4 776.5	6	9	I 6 081.5	10	6
I 4 407.7	8R	4R	I 4 786.5	6	8	I 6 090.2	10R	10
I 4 408.2	6R	1	I 4 796.9	7	8	I 6 111.7	10	9
I 4 408.5††	6R	10R	I 4 807.6	10	8	I 6 119.5	10R	8
I 4 416.6	10	I 4 851.5	9	8	I 6 199.2	8	8
I 4 421.6	8	5	I 4 864.8	10R	9	I 6 216.4	8	10
I 4 437.8	8	6	I 4 875.5	10R	10	I 6 230.8	10	9
I 4 441.7	7	8	I 4 881.6	10R	10	I 6 242.9	4	10
I 4 444.2	8	8	I 5 128.5	8	9	I 6 243.1	9	4
I 4 452.0	8	10	I 5 138.4	6	10	I 6 251.8	9	8
I 4 460.3	10R	10R	I 5 194.9	4	8	I 6 268.9	5	5
I 4 462.4	9	9	I 5 402.0	7	8	I 6 274.7	5	8
I 4 469.7	8	8	I 5 415.3	10	8	I 6 285.2	9	7
I 4 488.9	8	10	I 5 507.8	5	8	I 6 292.8	9	7
I 4 545.4	9	8	I 5 627.7	8	9	I 6 296.5	10	6
I 4 549.7	6	8	I 5 670.9	9	8	I 6 326.9	5	4
I 4 560.7	7	9	I 5 698.5	10R	10	I 6 452.4	4
I 4 571.8	6	10	I 5 703.6	10R	10	I 6 504.2	4	4
I 4 577.2	8	8	I 5 707.0	8R	9	I 6 531.4	10	6
I 4 580.4	8	9	I 5 727.0	10R	10	I 6 753.0	4
I 4 586.4	8	9	I 5 731.3	8	5	I 6 738.9	4
I 4 594.1	10R	10	I 5 737.1	7	7			

Control lines:	Interfering lines:	Control lines:	Interfering lines:
*Al 3961.5	*Al Au Bi Fe Mg	Co 4092.4	Ba Co Cr Fe Mn Mo
Fe 3222.1		*Fe 4045.8	*Al Bi Cd Co Cr Cu
Mg 3096.9		Mo 4277.3	
†Fe 3057.5	†Co K Ni W	**Cr 4371.3	**Al Bi Co Cr Fe Mo
Ni 3050.5		Fe 4045.8	
Ti 3106.2		Mo 4277.3	
3706.0	‡Ag Ba Ni Ti W	††Pb 4245.2	††Al Bi Co Cr Mn Mo
Cr 3120.4		W 4372.6	
Ti 3109.9		††Fe 4383.5	††Al Ba Be Co Cr Cs Fe
§Ti 3199.9	§Mo P	Mo 4381.7	

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS
YTTERBIUM

Yb

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 461.5	10R	3 192.9	3	8	4 180.8	10	5
2 642.5	1	8	3 289.4p	10	10	4 439.2	8	2
2 750.5	5	10	3 337.2	8	2	4 576.2	10	3
2 851.2	4	10	3 343.0	10	5	4 726.1	8	10
2 914.2	2	10	3 362.6	10	4	4 781.9	8
2 919.4	4	10	3 441.5	10	3	4 786.6	10	10
2 994.8	3	8	3 454.1	5	10	4 935.5	10
3 005.8	5	10	3 464.3	10	5	5 335.1	6	1
3 009.4	3	8	3 476.3	8	4	5 482.0	8
3 017.6	3	10	3 478.8	8	10	5 539.1	10
3 029.6	10	3 520.2	4	10	5 556.5	10	1
3 031.1	10	5	3 560.3	8	3	5 652.0	9
3 065.0	4	10	3 560.7	8	5	5 720.0	10
3 107.9	10	10R	3 619.8	5	8	5 837.1	8
3 117.8	4	10	3 694.2p	10	10	6 489.1	10	1
3 126.1	10	3 770.1	7	3	6 667.9	10
3 140.9	4	10	3 988.0p	10	10	6 799.7	10
3 153.9	3	10	4 135.1	4	8	7 699.5	10
3 189.1	3	8						

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

YTTRIUM

Y

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 367.2	10	II 4 177.5	10	10	5 581.9	5R	2
2 414.7	10	II 4 235.7	8	5	5 630.1	6R	2
2 422.2	4	8	4 302.3	10	3	5 663.0	7R	10
2 817.0	1	10	II 4 309.6	10	10	5 706.7	4R	2
2 946.0	10	4 348.8	9	3	II 5 728.9	4	2
3 129.9	3	8	II 4 358.7	7	10	II 5 781.7	4	2
3 173.1	4	10	II 4 375.0§	10	10	5 945.7	4	1
II 3 195.6	8	10	II 4 398.0	8	10	6 009.2	5	3
II 3 200.3	7	10	II 4 422.6	10	10	I 6 023.4	4	2
II 3 203.3	7	10	4 506.0	8	3	I 6 138.5	4	2
II 3 216.7	10	10	4 527.3	8	5	I 6 191.7	7	4
II 3 242.3	10	10	I 4 643.7pF	8	5	I 6 222.6	6	2
II 3 327.9	10	10	I 4 674.8pF	8	5	I 6 435.0	8	8
3 362.0	5	10	II 4 682.3	5	10	6 538.6	4	2
3 496.1	9	10	4 732.4F	3	3	II 6 613.8	5	3
3 549.0	10	10	II 4 823.3	4	10	6 664.4	4
3 584.5	4	10	4 839.9F	9	10	I 6 687.6	5	1
I 3 592.9	8	4	II 4 854.9	10	10	6 700.7	4	1
II 3 600.7*	10	10	4 859.8F	6	3	6 736.0	4
II 3 611.1	10	10	II 4 883.7	10	10	I 6 793.7	4	1
I 3 668.5	3	10	II 4 900.1	10	10	II 6 795.4	4	1
3 710.3†	10	10	II 5 087.4	10	10	6 845.2	4
II 3 747.6	6	10	II 5 123.2	6	4	6 887.2	4
II 3 774.3p†	10	10	II 5 200.4	10	10	6 950.3	4
II 3 788.7p	9	10	II 5 205.7	10	10	II 6 951.7	4
II 3 950.4	10	10	II 5 402.8	5	8	6 979.9	4
II 3 982.6	10	10	5 466.5	10	3	7 191.7	3
I 4 047.7	7	4	II 5 497.4	5	8	II 7 264.2	4
I 4 102.4	9R	8	5 503.5	8	2	7 346.3	4
I 4 128.3	8R	8	II 5 509.9	9	4	II 7 450.2	4
I 4 142.9	8R	8	II 5 521.6	6R	3	II 7 881.7	2
I 4 167.5	8	4	5 527.6	6R	3			

Control lines: Interfering lines:

*Co 3594.9 *Al Co Cu Mo

Cr 3595.5

†Ca 3736.9 †Co Cr Fe Mg Mo

Fe 3767.2

‡Ti 3786.1 ‡Co Mg Mn Ti

Control lines: Interfering lines:

V 3750.9

§Cr 4337.6

Mo 4377.8

Fe 4337.1

§Al Cd Co Cr Cu Fe

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

ZINC

Zn

Wavelength	Arc Spark	Wavelength	Arc Spark	Wavelength	Arc Spark
II 2 025.5P	2R	I 3 072.1	10R 10	I 5 775.6	
II 2 061.9pS ₁	4R	I 3 075.9S ₆	8R	I 5 777.1	
II 2 100.0	5	I 3 282.3pS ₇	8R	II 5 894.4	10
12 138.5PS ₂ N ₁	3R 2R	I 3 302.6p*S ₂ N ₂	8R	II 6 021.3	10
2 246.8	4	I 3 302.9S ₉ N ₄	8R	II 6 102.5	10
2 393.8	1	I 3 340. up	10R	II 6 111.6	10
I 2 491.5	1	I 3 345.6S ₁₁	8R	II 6 214.7	10
II 2 502.0S ₃	10	I 3 345.9		I 6 237.9	
II 2 558.0S ₄ N ₂	8 10	II 3 806.4		I 6 239.2	
I 2 569.9	6R 1	II 3 840.3		I 6 362.4	10
I 2 582.5	8R	4 057.9	6	I 6 479.0	
I 2 608.6	8R	I 4 629.8	8	II 6 483.0	10
I 2 670.6	4	I 4 680.1S ₁₂	10R	I 6 928.4	
I 2 684.2		I 4 722.2	10R	I 6 938.5	
I 2 712.5		I 4 810.5N ₄	10R	I 6 943.4	
I 2 756.5	6R	II 4 911.6	10	7 026.1	
I 2 770.9	8R	II 4 924.0	10	7 264.2	
I 2 771.0	6R	I 5 308.6		7 338.9	
I 2 800.0	8R	I 5 310.2		II 7 478.7	10
I 2 800.8	7R 10	I 5 310.9		II 7 588.6	10
I 3 018.4	6	I 5 772.2		II 7 799.1	
I 3 035.8S ₃	10R				

Control lines: Interfering lines:
*Fe 3407.5 *Cr Na Pt Sr
Pt 3042.6

Control lines: Interfering lines:
†Mo 3358.1 †Ca Hg Mn Mo
Ti 3239.0

Control lines:
S₁Pb 2052.0
S₂Pb 2175.6
S₃Pb 2388.8
S₄Pb 2628.3
S₅Pb 2980.3
2926.8
S₆Pb 3119.1
S₇Pb 3220.5
S₈Pb 3220.5
3362.4
2657.2

Control lines:
S₉Pb 3220.5
3262.4
2657.2
S₁₀Pb 3220.5
3262.4
S₁₁Pb 3220.5
S₁₂Pb 5043.1
N₁Pb 2190.0
2187.9
2176.5

Control lines:
2159.6
2111.8
N₂Pb 2562.4
N₂Sn 3352.3
2175.0
N₁Pb 3119.2
N₂Sn 3330.6
Pb 3220.5
N₁Pb 5005.5

For explanation of control and interfering line symbols see page 365.

TABLE IV (Continued)
PRINCIPAL LINES BY ELEMENTS

ZIRCONIUM

Zr

Wavelength	Arc	Spark	Wavelength	Arc	Spark	Wavelength	Arc	Spark
2 449.8	4	3	II 3 572.5p	10	10	I 4 739.5p	9	5
2 568.9	5	6	II 3 576.9	7	10	I 4 772.3p	8	4
2 571.4	6	8	3 611.9	4	8	I 4 815.6p	6	3
2 678.6	5	5	II 3 614.8	6	10	4 909.6	6
2 734.8	5	5	II 3 674.7	6	10	4 959.4	5
2 752.2	4	3	3 698.2	6	10	5 046.6	5	1
2 844.6	4	4	3 709.3	6	10	5 064.9	5	1
2 876.0	4	3 751.6	6	10	5 155.4	4	1
2 969.0	6	3	3 796.5	3	8	5 191.6	4
2 985.4	4	1	II 3 836.0	7	2	5 311.4	5	1
3 011.7	5	1	I 3 890.3	7	4	5 385.1	7	1
3 029.5	6	1	3 915.9	5	10	5 502.1	6	1
3 106.6	6	4	II 3 958.2	8	10	5 528.4	5	1
I 3 182.9	7	5	3 991.1	9	10	5 620.1	6	1
II 3 273.1	8	9	II 3 999.0	9	10	I 5 680.9	6	1
II 3 279.3	8	4	4 048.7	7	9	5 879.8	8	1
3 284.7	8	4	I 4 081.2	9	5	I 6 127.4	7	1
3 356.1	8	4	4 149.2	10	10	I 6 143.2	7	1
II 3 357.3	8	4	4 156.2	8	9	6 299.6	7	1
II 3 392.0P*	10	10	4 161.2	7	8	6 313.0	7	1
II 3 430.5	7	9	I 4 227.8	8	4	6 470.2	6	1
II 3 438.2p†	10	10	I 4 282.2	6	6	6 489.6	6	1
3 463.0	4	10	4 347.9	7	3	6 769.1	6
3 479.4	7	9	4 379.8	8	10	6 847.0	4
3 481.2	8	10	4 443.0	6	9	6 953.8	5
II 3 496.2p‡	10	10	I 4 535.8	8	3	6 990.8	5
3 505.5	4	8	4 575.5	7	3	I 7 097.7	4
II 3 505.7	5	8	4 634.0	7	2	I 7 169.1	6
I 3 519.6P	8	3	I 4 687.8p	10	5	7 280.3	4
3 542.6	5	10	4 688.5	7	4	7 318.2	3
II 3 556.6	9	10	I 4 710.1p	10	5			

Control lines:

Interfering lines:

Control lines:

Interfering lines:

*Co 3409.2

*Bi Fe Hg Mo Ni

Ni 3446.3

Ni 3380.6

‡Ba 4130.6

‡Cd Co Ga M

Ti 3387.8

Ba 4166.0

†Fe 3581.2

†Co Fe Mo Ni V

Co 3409.2

Mn 2933.1

Fe 3558.5

For explanation of control and interfering line symbols see page 365.

TABLE V
SPARK SPECTRUM OF AIR
(A41, A36, A22)

Wavelength	In- tensity	Ele- ment	Wavelength	In- tensity	Ele- ment	Wavelength	In- tensity	Ele- ment
2 287.9	1	N	3 577.2	1	—	4 093.00	2	O
2 318.5	1	O	3 589.0	1	—	4 097.2	3	N
2 382.1	2	—	3 594.6	1	—	4 103.8	2	N
2 395.62	1	—	3 609.8	1	—	4 105.00	3	O
2 399.4	1	—	3 639.6	3	—	4 110.84	2	O
2 404.9	2	—	3 702.9	1	—	4 112.09	1	O
2 406.9	1	—	3 707.3	1	O	4 114.0	0	O
2 433.6	1	O	3 709.2	1	O	4 119.3	4	O
2 445.5	1	O	3 712.7	2	O	4 120.5	2	O
2 507.2	2	—	3 727.34	4	O	4 121.5	2	O
2 514.5	1	—	3 729.3	1	N	4 124.1	2	O
2 599.5	2	—	3 749.51	5	O	4 129.5	1	O
2 739.8	1	—	3 754.5	1	O	4 132.88	2	O
2 746.7	1	—	3 759.8	1	O	4 133.70	2	N
2 749.0	1	—	3 770.9	1	N	4 142.2	1	O
2 755.9	2	—	3 804.0	1	O	4 143.7	1	O
2 795.5	1	—	3 830.7	1	N	4 145.90	3	N
2 858.3	1	—	3 839.1	2	N	4 153.5	3	O
2 927.5	1	—	3 842.8	1	N	4 169.36	1	O
3 007.0	1	O	3 845.1	O	N	4 176.2	2	N
3 047.0	1	—	3 848.04	1	O	4 185.5	4	O
3 059.15	2	—	3 850.6	1	N	4 189.8	6	O
3 130.1	1	—	3 851.2	1	O	4 199.3	0	N
3 135.3	1	O	3 856.7	1	N	4 206.7	2	N
3 139.3	2	O	3 864.6	1	O	4 211.1	1	N
3 158.7	1	—	3 882.3	2	O	4 223.3	1	N
3 265.2	1	O	3 893.3	1	N	4 228.0	2	N
3 288.9	1	—	3 907.6	1	O	4 236.8	3	N
3 301.9	1	—	3 909.1	1	N	4 241.75	2	N
3 312.5	1	O	3 912.1	3	O	4 253.7	2	O
3 318.8	1	—	3 919.10	6	N	4 266.4	2	N
3 320.7	2	O	3 940.2	1	N	4 275.9	1	N
3 325.0	1	O	3 945.1	1	O	4 303.7	1	O
3 329.5	2	N	3 947.45	1	O	4 317.11	3	O
3 331.8	2	N	3 954.4	1	O	4 319.62	3	O
3 344.8	1	—	3 955.0	4	N	4 325.7	1	O
3 354.08	1	O	3 973.30	4	O	4 327.5	1	O
3 365.8	1	N	3 982.76	2	O	4 328.5	1	O
3 367.3	1	N	3 995.1	10	N	4 331.04	1	N
3 370.9	1	N	4 014.0	1	O	4 331.9	1	O
3 374.0	2	N	4 025.7	1	N	4 336.8	2	O
3 377.2	2	O	4 034.9	2	N	4 345.54	3	O
3 390.3	2	O	4 041.3	3	N	4 347.44	2	O
3 408.3	2	O	4 057.8	1	N	4 348.0	2	N
3 437.32	3	N	4 063.2	1	N	4 349.40	4	O
3 450.9	1	—	4 069.90	8	O	4 351.3	2	O
3 471.2	2	—	4 072.25	8	O	4 361.6	0	N
3 491.9	2	—	4 075.93	8	O	4 366.87	3	O
3 514.8	1	—	4 078.9	2	O	4 369.2	1	O
3 560.6	1	—	4 085.20	2	O	4 371.4	1	N
3 570.3	1	—	4 089.1	1	O	4 379.6	1	N

TABLE V (Continued)
SPARK SPECTRUM OF AIR

Wavelength	In- tensity	Ele- ment	Wavelength	In- tensity	Ele- ment	Wavelength	In- tensity	Ele- ment
4 396.0	1	O	4 803.3	5	N	4 480.1	1	N
4 401.2	1	N	4 805.9	1	N	5 495.7	2	N
4 414.9	6	O	4 810.3	2	N	5 526.2	2	N
4 417.0	5	O	4 856.8	1	O	5 530.2	3	N
4 425.9	1	N	4 860.3	1	N	5 535.2	5	N
4 430.1	1	N	4 871.6	0	O	5 543.4	3	N
4 432.4	2	N	4 879.7	1	N	5 552.0	2	N
4 434.0	0	N	4 890.9	0	O	5 566.0	0	N
4 443.3	1	O	4 895.3	1	N	5 592.3	0	O
4 447.04	6	N	4 906.8	1	O	5 645.6	1	N
4 452.4	2	O	4 924.6	2	O	5 666.6	5	N
4 460.1	1	N	4 934.8	1	N	5 675.9	3	N
4 465.4	2	O	4 941.0	1	N	5 679.5	10	N
4 467.8	2	O	4 942.5	1	N	5 686.2	3	N
4 469.4	1	O	4 943.0	1	O	5 710.7	2	N
4 477.7	1	N	4 955.0	1	O	5 730.6	2	N
4 507.62	2	N	4 964.7	0	N	5 747.5	1	N
4 514.8	2	N	4 987.4	1	N	5 767.4	2	N
4 529.9	2	N	4 991.3	1	N	5 927.8	4	N
4 544.8	1	N	4 994.4	3	N	5 931.8	7	N
4 552.5	2	N	5 001.4	6	N	5 940.5	1	N
4 590.93	3	O	5 005.2	6	N	5 941.6	10	N
4 596.12	3	O	5 007.4	3	N	5 952.4	4	N
4 601.48	4	N	5 010.6	2	N	6 158.1	0	O
4 607.14	4	N	5 016.4	2	N	6 171.0	2	O
4 609.4	1	N	5 022.9	1	N	6 284.3	1	N
4 613.84	3	N	5 025.7	2	N	6 341.5	0	N
4 621.39	4	N	5 045.1	2	N	6 358.1	0	N
4 630.53	10	N	5 061.8	0	N	6 379.3	2	N
4 634.0	1	N	5 073.5	0	N	6 456.0	0	O
4 638.8	2	O	5 143.6	0	O	6 482.0	5	N
4 640.5	1	N	5 160.1	0	O	6 563.2	3	H
4 641.8	3	O	5 172.0	1	N	6 610.4	6	N
4 643.1	4	N	5 173.4	1	N	6 654.8	2	—
4 649.1	4	O	5 175.9	2	N	6 887.6	1	—
4 650.8	2	O	5 179.4	1	N	6 965.9	1	A
4 654.5	1	N	5 183.2	0	O	7 067.6	0	A
4 661.6	5	O	5 185.1	0	N	7 157.4	9	O
4 674.9	1	N	5 190.6	1	N	7 384.5	1	A
4 676.2	3	O	5 206.5	1	O	7 424.0	8	N
4 699.2	3	O	5 281.7	0	N	7 442.7	10	N
4 703.1	0	O	5 320.5	1	N	7 468.7	10	N
4 705.1	1	N	5 325.1	0	O	7 479.0	0	O
4 705.4	3	O	5 328.6	0	N	7 505.8	0	A
4 709.9	2	O	5 338.7	1	N	7 515.2	0	A
4 718.4	2	N	5 341.2	1	N	7 635.7	1	A
4 735.7	1	N	5 351.2	0	N	7 772.1	10	O
4 751.2	1	O	5 356.4	0	N	7 774.3	7	O
4 764.6	1	N	5 411.5	1	N	7 775.6	6	O
4 774.2	1	N	5 452.1	1	N	7 947.8	4	O
4 779.8	2	N	5 454.1	1	N	7 951.1	3	O
4 788.2	4	N	5 462.8	1	N	7 952.3	2	O

TABLE VI
PRINCIPAL LINES BY ELEMENTS (*Discharge Spectrum*)

+ indicates secondary standards (see Neon)

(A40, A36, A23)

ARGON

A

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
2 515.5B	8	3 729.3B	9	4 259.4	9
2 516.7B	8	3 850.6B	9	4 266.3	8
2 647.5B	8	3 928.6B	8	I 4 272.2	8
2 708.3B	8	I 4 044.4	8	4 277.5B	8
2 744.8B	8	4 104.0B	9	I 4 300.1	8
2 753.8B	8	I 4 158.6	9	4 348.0B	10
3 491.6B	8	I 4 191.0	8	4 426.0B	8
3 576.7B	8	I 4 198.3	8	I 4 510.7	8
3 588.5B	9	I 4 200.7	9	4 806.0B	8

BROMINE

Br

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
3 891.6	8	4 472.6	8	4 767.1	8
3 914.3	10	4 477.8	10	4 785.5p	10
3 924.1	8	4 525.6	8	4 816.7p	8
3 955.4	8	4 542.9	8	5 238.3	8
3 980.4	10	4 622.7	8	5 332.0	10
3 986.5	8	4 678.7	8	5 589.9	8
4 179.6	8	4 704.8	10	6 149.7	10
4 365.6	8	4 719.8	8	6 350.8	10
4 441.7	8	4 742.7	8		

CHLORINE

Cl

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
2 580.7	8	3 845.4	8	4 343.7	10
2 617.0	8	3 845.7	8	4 363.3	8
3 320.5	8	3 851.0	10	4 379.9	8
3 329.0	8	3 851.5	8	4 389.8	8
3 340.3	8	3 861.0	10	4 794.5p	10
3 392.8	8	4 241.3	8	4 810.0p	9
3 833.4	8	4 253.4	9	4 819.4p	9

TABLE VI (Continued)
 PRINCIPAL LINES BY ELEMENTS (*Discharge Spectrum*)

FLUORINE

F

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
3 501.9	8	4 103.4	10	I 6 834.3	8
3 503.3	9	4 246.3	10	I 6 856.1p	10
3 505.8	10	4 299.1	8	I 6 902.5p	9
4 025.1	10	4 446.8	10	I 7 037.6	9

HELIUM

He

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
I 2 385.4	5	I 3 187.7	8	I 4 471.5	6
I 2 511.2	5	I 3 203.2	8	I 5 875.6p	10
I 2 733.2	7	I 3 888.7P	10	I 6 678.2	6
I 2 945.1	6	I 4 026.2	5	I 7 065.2	5

HYDROGEN

H

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
4 631.9	9	6 018.3	9	6 327.0	8
4 634.0	9	6 031.9	10	6 562.9p	---
4 861.3p	---	6 079.8	9	6 935.8	10
4 928.7	9	6 121.8	10	6 940.4	10
5 812.6	9	6 135.4	8	6 962.6	10
5 975.4	9	6 224.8	9	7 072.0	10

TABLE VI (Continued)

PRINCIPAL LINES BY ELEMENTS (*Discharge Spectrum*)

IODINE

I

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
2 062.1p	10	4 434.3	10	5 269.4	10
3 194.0	8	4 453.0	10	5 309.0	8
3 275.0	10	4 512.6	8	5 338.2	10
3 288.3	10	4 528.1	8	5 345.1	10
3 303.0	10	4 574.3	10	5 369.7	10
3 342.5	8	4 632.4	10	5 405.3	10
3 350.1	8	4 640.8	10	5 407.3	10
3 461.0	8	4 606.5	10	5 435.7	10
3 481.8	8	4 675.6	10	5 437.9	8
3 498.0	8	4 708.0	8	5 464.7p	10
3 561.2	8	4 730.5	8	5 491.5	8
3 583.3	8	4 763.4	10	5 493.3	8
3 686.6	8	4 806.5	8	5 496.9	10
3 688.3	8	4 850.4	10	5 625.7	10
3 724.9	8	4 862.3	10	5 678.1	10
3 741.9	8	4 896.7	10	5 690.8	10
3 808.2	10	4 916.9	10	5 710.4	10
3 897.4	10	4 987.0	10	5 738.5	10
3 931.1	10	5 119.3	10	5 739.5	10
3 940.1	10	5 161.2p	10	5 774.8	10
4 128.7	10	5 204.1	10	5 893.8	8
4 221.1	10	5 216.2	10	5 950.1	10
4 342.1	8	5 234.6	10	6 082.3	10
4 399.0	8	5 245.6	10	6 127.4	8
4 410.1	10	5 265.2	10		

TABLE VI (Continued)
 PRINCIPAL LINES BY ELEMENTS (*Discharge Spectrum*)
KRYPTON
Kr

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
2 282.8	10	2 456.1	8	3 783.2	10
2 287.7	10	2 457.7	8	3 906.2	8
2 301.0	8	2 464.8	8	3 920.4	8
2 311.9	8	2 506.6	9	4 057.0	8
2 314.1	8	2 712.4	8	4 065.1	8
2 315.4	9	3 207.8	8	4 088.4	8
2 316.2	10	3 245.7	10	4 274.0	10
2 329.2	8	3 264.8	8	4 318.6	8
2 344.5	8	3 320.3	10	4 319.6	10
2 359.9	10	3 325.7	9	4 355.5	10
2 362.9	8	3 488.6	8	4 362.6	9
2 371.5	8	3 507.4	9	4 376.1	10
2 375.6	10	3 607.9	9	4 453.9	10
2 394.0	8	3 631.9	10	4 463.7	10
2 398.3	10	3 654.0	10	4 502.2	9
2 413.9	9	3 669.0	9	4 624.3	10
2 415.0	9	3 718.0	10	4 671.2	10
2 418.2	10	3 718.6	8	5 570.3p	10
2 420.2	10	3 741.7	10	5 870.9p	10
2 426.4	9	3 744.8	9	7 587.4	10
2 428.3	10	3 778.1	10	7 601.6	10

NEON

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
2 647.4	8	5 037.7	8	+6 074.338	9
3 369.8	8	5 144.9	8	+6 096.163	8
3 417.9	8	5 145.0	8	+6 163.594	8
3 472.6	8	5 330.8	10	6 217.3	9
3 520.5	10	5 341.1	10	+6 266.495	10
3 568.7	8	5 343.3	9	+6 304.789	5
3 593.5	8	5 358.0	10	+6 334.428	9
3 694.4	9	+5 400.562p	10	+6 382.991	10
3 713.3	9	5 502.8	8	6 402.3p	10
4 537.8	10	5 656.7	8	+6 506.528	10
4 540.4	8	5 719.2	9	+6 532.883	5
4 575.9	10	5 748.3	9	+6 598.953	8
4 704.4	10	5 764.4	9	6 678.3	8
4 708.9	10	5 804.5	9	+6 717.043	5
4 710.1	8	5 820.2	9	6 929.466	9
4 712.1	8	+5 852.488	10	+7 032.411	6
4 715.3	10	5 872.8	9	+7 173.938	10
4 752.7	8	+5 881.895	10	+7 245.165	10
4 788.9	10	+5 944.834	9	7 438.9	8
4 790.2	8	5 965.4	10	+7 535.784	8
4 884.9	8	5 974.6	9	7 544.1	8
4 957.0	8	+5 975.534	8	7 943.2	8
5 005.2	8	+6 029.987	9		

TABLE VI (Continued)

PRINCIPAL LINES BY ELEMENTS (*Discharge Spectrum*)

XENON

Xe

Wavelength	Geissler Tube	Wavelength	Geissler Tube	Wavelength	Geissler Tube
2 475.9	10	4 193.5	8	4 624.3p	9
2 605.6	10	4 238.2	10	4 671.2p	10
2 677.2	8	4 245.4	10	4 734.2	8
3 285.8	8	4 330.5	10	4 844.3	10
3 624.1	8	4 393.2	10	4 862.5	8
3 781.0	10	4 395.7	10	5 292.2	10
3 877.8	8	4 448.1	10	5 314.0	8
3 922.5	10	4 462.2	10	5 339.4	9
3 950.6	8	4 501.0p	8	5 372.4	8
3 951.0	10	4 540.9	8	5 419.2	10
4 078.8	10	4 545.2	8	5 439.0	8
4 180.0	10	4 585.5	10	6 557.0	10
4 193.1	8	4 603.0	10		

TABLE VII

FRAUNHOFER LINES IN THE SUN'S SPECTRUM

(A58, A40, A36, A23)

WAVELENGTHS OF THE FRAUNHOFER LINES

Line	Due to	Wavelength	Line	Due to	Wavelength	Line	Due to	Wavelength
U	Fe	2 947.9	N	Fe	3 581.21	b ₄	{ Fe	5 167.51
t	Fe	2 994.4	M	Fe	3 727.64		{ Mg	5 167.33
T	Fe	3 021.07	L	Fe	3 820.44	b ₂	Mg	5 172.70
s	Fe	3 047.62	K	Ca	3 933.68	b ₁	Mg	5 183.62
S ₁ {	{ Fe	3 100.68	H	Ca	3 968.49	E ₂	Fe	5 269.56
	{ Fe	3 100.32	h	H	4 101.75	D ₂	Na	5 889.98
S ₂ {	{ Fe	3 099.94	g	Ca	4 226.74	D ₁	Na	5 895.94
R	{ Ca	3 181.28	G	{ Fe	4 307.91	C	H	6 562.82
	{ Ca	3 179.34		{ Ca	4 307.75	B	O	6 869.96
Q	Fe	3 286.77	G'	H	4 340.48	A	{ O	7 621.
P	Ti	3 361.19	F	H	4 861.34		{ O	7 594.
O	Fe	3 441.02						

TABLE VIII

CONVERSION TABLES—WAVELENGTH—FREQUENCY

A. Visible data, wavelength in $m\mu$ to frequency in f. (Note that the table may also be read as frequency to wavelength, i.e., 500 $m\mu$ = 600 f, and 500 f = 600 $m\mu$.)

	0	1	2	3	4	5	6	7	8	9
400	750.0	748.1	746.2	744.6	742.6	740.7	738.9	737.1	735.3	733.5
410	731.7	729.9	728.2	726.4	724.5	722.8	721.0	719.4	717.7	715.9
420	714.3	712.6	710.8	709.2	707.5	705.8	704.2	702.5	700.9	699.3
430	697.7	696.1	694.4	692.7	691.2	689.7	688.0	686.5	684.9	683.4
440	681.8	680.3	679.7	677.2	675.7	674.2	672.6	670.1	669.6	668.2
450	666.7	665.2	663.7	662.2	660.8	659.3	657.9	656.5	655.0	653.6
460	652.2	650.8	649.4	647.9	646.6	645.2	643.7	642.4	641.0	639.7
470	638.3	636.9	635.6	634.2	632.9	631.6	630.2	628.9	627.6	626.3
480	625.0	623.7	622.4	621.1	619.8	618.6	617.3	616.0	614.8	613.5
490	612.2	611.0	609.8	608.5	607.3	606.1	604.8	603.6	602.4	601.2
500	600.0	598.8	597.6	596.4	595.2	594.1	592.9	591.7	590.6	589.4
510	588.2	587.1	585.9	584.8	583.6	582.5	581.4	580.3	579.2	578.0
520	576.9	575.8	574.7	573.6	572.5	571.4	570.3	569.3	568.2	567.1
530	566.0	565.0	563.9	562.9	561.8	560.7	559.7	558.7	557.6	556.6
540	555.6	554.5	553.5	552.5	551.5	550.5	549.5	548.4	547.4	546.4
550	545.5	544.5	543.5	542.5	541.5	540.5	539.5	538.6	537.6	536.6
560	535.7	534.8	533.8	532.9	531.9	531.0	530.0	529.1	528.2	527.2
570	526.3	525.4	524.5	523.6	522.6	521.7	520.8	519.9	519.0	518.1
580	517.2	516.4	515.5	514.6	513.7	512.8	511.9	511.0	510.2	509.3
590	508.5	507.6	506.8	505.9	505.0	504.2	503.3	502.5	501.7	500.8
600	500.0	499.2	498.3	497.5	496.7	495.9	495.0	494.2	493.4	492.6
610	491.8	491.0	490.2	489.4	488.6	487.8	487.0	486.2	485.4	484.7
620	483.9	483.1	482.3	481.5	480.7	480.0	479.5	478.5	477.7	476.9
630	476.2	475.4	474.7	473.9	473.2	472.4	471.7	471.0	470.2	469.4
640	468.7	468.0	467.3	466.6	465.8	465.1	464.4	463.7	463.0	462.2
650	461.5	460.8	460.1	459.4	458.7	458.0	457.3	456.6	455.9	455.2
660	454.6	453.9	453.2	452.5	451.8	451.1	450.5	449.8	449.1	448.4
670	447.7	447.1	446.4	445.7	445.1	444.4	443.8	443.1	442.4	441.8
680	441.2	440.5	439.9	439.2	438.6	438.0	437.3	436.6	436.0	435.4
690	434.8	434.2	433.5	432.9	432.3	431.7	431.0	430.4	429.8	429.2
700	428.6	428.0	427.4	426.7	426.1	425.5	424.9	424.3	423.7	423.1
710	422.5	421.9	421.3	420.8	420.2	419.6	419.0	418.4	417.8	417.2
720	416.7	416.1	415.5	414.9	414.4	413.8	413.2	412.7	412.1	411.5
730	411.0	410.4	409.8	409.3	408.7	408.2	407.6	407.1	406.5	406.0
740	405.4	404.9	404.3	403.8	403.2	402.7	402.1	401.6	401.1	400.5
750	400.0	399.5	398.9	398.4	397.9	397.4	396.8	396.3	395.8	395.3
760	394.7	394.2	393.7	393.2	392.7	392.2	391.6	391.1	390.6	390.1
770	389.6	389.1	388.6	388.1	387.6	387.1	386.6	386.1	385.6	385.1
780	384.6	384.1	383.6	383.1	382.7	382.2	381.7	381.2	380.7	380.2
790	379.7	379.3	378.8	378.3	377.8	377.4	376.9	376.4	375.9	375.4

TABLE VIII (Continued)

CONVERSION TABLES—WAVELENGTH—FREQUENCY

B. Photographic Range. Note that $m\mu$ and f are interconvertible (either column may be used and values of the other term read in the other column), but the relation between wavelength, frequency, and wavenumber must be read from left to right as indicated. Angstrom values are obtained by multiplying $m\mu$ values by 10.

λ or ν \rightleftharpoons ν or λ			λ or ν \rightleftharpoons ν or λ		
Wavelength $m\mu$	λ	ν	Wavelength $m\mu$	λ	ν
		Frequency f			Frequency f
		\rightleftharpoons			\rightleftharpoons
		Wavenumber cm^{-1}			Wavenumber cm^{-1}
1500	200.0	6,667	650	461.5	15,385
1475	203.4	6,780	625	480.0	16,000
1450	206.9	6,897	600	500.0	16,667
1425	210.5	7,018	575	521.7	17,391
1400	214.3	7,143	550	545.5	18,182
1375	218.2	7,273	525	571.4	19,048
1350	222.2	7,407	500	600.0	20,000
1325	226.4	7,547	475	631.0	21,053
1300	230.8	7,692	450	666.7	22,222
1275	235.3	7,843	440	681.8	22,727
1250	240.0	8,000	430	697.7	23,266
1225	244.9	8,163	420	714.3	23,810
1200	250.0	8,333	410	731.7	24,390
1175	255.3	8,511	400	750.0	25,000
1150	260.9	8,696	390	769.2	25,641
1125	266.7	8,889	380	789.5	26,316
1100	272.7	9,091	370	810.8	27,027
1075	279.1	9,302	360	833.3	27,778
1050	285.7	9,524	350	857.1	28,571
1025	292.7	9,756	340	882.4	29,412
1000	300.0	10,000	330	909.1	30,303
975	307.7	10,256	320	937.5	31,250
950	315.0	10,526	310	967.7	32,258
925	324.3	10,811	300	1000.0	33,333
900	333.3	11,111	290	1034.5	34,483
875	342.9	11,429	280	1071.4	35,714
850	352.9	11,765	270	1111.1	37,037
825	363.6	12,121	260	1153.8	38,462
800	375.0	12,500	250	1200.0	40,000
775	387.1	12,903	240	1250.0	41,667
750	400.0	13,333	230	1304.3	43,478
725	413.8	13,793	220	1363.6	45,455
700	428.6	14,286	210	1438.5	47,619
675	444.4	14,815	200	1500.0	50,000

C. Correction for Refractive Index of Light in Air. If it is desirable to correct for the refractive index of light in air (reduce to vacuum conditions), the following additions to the wavelength value should be made prior to converting to wavenumber or frequency.

λ $m\mu$	$+n$	λ $m\mu$	$+n$	λ $m\mu$	$+n$
1,000	0.2739	700	0.1927	400	0.1127
900	0.2468	600	0.1658	300	0.0872
800	0.2197	500	0.1391	200	0.0651

TABLE IX
CONVERSION TABLES
(B55, B48, B20, B32)

Extinction (E)—Transmission percentage ($T \times 100$)—Log extinction ($\log E$)—
Angular sector openings—Prism rotation

The 90° sector values are for rotating sectors of 90° opening as equivalent to 100 per cent. For sectors with 180° maximum opening these values should be doubled. For transmissions of 10 per cent and less use 1/10 of the corresponding 100 per cent values.

The polarizing angle relation is based on

$$E = 2 \times \log \tan \theta \text{ (for a } 45^\circ \text{ extinction angle)}$$

$\log E$	E	Percent- age Trans- mitted	90° Sector Angle	Polarizing Angle (45° extinction)	$\log E$	E	Percent- age Trans- mitted	90° Sector Angle	Polarizing Angle (45° extinction)
-∞	0.00	100.0	90.0	45.0	-0.40	0.35	44.7	40.2	33.8
-2.00	0.01	97.8	88.0	44.7	-0.44	0.30	43.7	39.3	33.5
-1.70	0.02	95.5	86.0	44.3	-0.43	0.37	42.7	38.4	33.2
-1.52	0.03	93.3	84.0	44.0	-0.42	0.38	41.7	37.5	32.8
-1.40	0.04	91.2	82.1	43.7	-0.41	0.39	40.7	36.6	32.6
-1.30	0.05	89.1	80.2	43.3	-0.40	0.40	39.8	35.8	32.3
-1.22	0.06	87.0	78.3	43.0	-0.39	0.41	38.9	35.0	32.0
-1.16	0.07	85.1	76.6	42.7	-0.38	0.42	38.0	34.2	31.7
-1.10	0.08	83.1	74.8	42.4	-0.37	0.43	37.2	33.5	31.3
-1.05	0.09	81.2	73.0	42.0	-0.36	0.44	36.3	32.7	31.1
-1.00	0.10	79.4	71.5	41.7	-0.35	0.45	35.5	31.9	30.8
-0.96	0.11	77.6	69.9	41.4	-0.34	0.46	34.7	31.2	30.5
-0.92	0.12	75.8	68.3	41.1	-0.33	0.47	33.9	30.5	30.2
-0.89	0.13	74.2	66.8	40.8	-0.32	0.48	33.1	29.8	29.9
-0.85	0.14	72.5	65.3	40.4	-0.31	0.49	32.4	29.2	29.6
-0.82	0.15	70.8	63.8	40.4	-0.30	0.50	31.6	28.4	29.3
-0.80	0.16	69.2	62.3	39.6	-0.29	0.51	30.9	27.8	29.1
-0.77	0.17	67.6	60.8	39.4	-0.28	0.52	30.2	27.2	28.8
-0.75	0.18	66.1	59.5	39.0	-0.27	0.53	29.5	26.6	28.5
-0.72	0.19	64.6	58.2	38.3	-0.27	0.54	28.8	25.9	28.3
-0.70	0.20	63.1	56.8	40.1	-0.26	0.55	28.2	25.4	28.0
-0.68	0.21	61.6	55.4	38.1	-0.25	0.56	27.5	24.8	27.7
-0.66	0.22	60.3	54.3	37.9	-0.24	0.57	26.9	24.2	27.4
-0.64	0.23	59.0	53.1	37.5	-0.24	0.58	26.3	23.6	27.2
-0.62	0.24	57.6	51.9	37.2	-0.23	0.59	25.7	23.0	26.9
-0.60	0.25	56.3	50.7	36.8	-0.22	0.60	25.1	22.6	26.6
-0.59	0.26	55.0	49.5	36.6	-0.21	0.61	24.5	22.1	26.3
-0.57	0.27	53.7	48.3	36.2	-0.21	0.62	24.0	21.6	26.1
-0.55	0.28	52.4	47.2	35.9	-0.20	0.63	23.4	21.1	25.8
-0.54	0.29	51.3	46.2	35.6	-0.20	0.64	22.9	20.6	25.6
-0.52	0.30	50.1	45.1	35.3	-0.19	0.65	22.4	20.2	25.3
-0.51	0.31	49.0	44.2	35.0	-0.18	0.66	21.9	19.7	25.1
-0.50	0.32	47.9	43.2	34.7	-0.18	0.67	21.4	19.3	24.8
-0.48	0.33	46.8	42.2	34.4	-0.17	0.68	20.9	18.8	24.6
-0.47	0.34	45.7	41.2	34.1	-0.16	0.69	20.4	18.4	24.3

CONVERSION TABLES

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TABLE IX (Continued)

CONVERSION TABLES

$\log E$	E	Percent- age Trans- mitted	90° Sector Angle	Polarizing Angle (45° extinction)	$\log E$	E	Percent- age Trans- mitted	90° Sector Angle	Polarizing Angle (45° extinction)
	0.70	20.0	18.0	24.1	0.06	1.15	7.08		14.9
-0.15	0.71	19.5	17.6	23.8		1.16	6.92		14.7
	0.72	19.1	17.2	23.6		1.17	6.76		14.6
-0.14	0.73	18.6	16.8	23.3	0.07	1.18	6.61		14.4
-0.13	0.74	18.2	16.4	23.1		1.19	6.46		14.3
	0.75	17.8	16.0	22.9	0.08	1.20	6.31		14.1
-0.12	0.76	17.4	15.7	22.6		1.21	6.16		14.0
	0.77	17.0	15.3	22.4		1.22	6.03		13.8
-0.11	0.78	16.6	14.9	22.2	0.09	1.23	5.90		13.6
	0.79	16.2	14.6	21.9		1.24	5.76		13.5
-0.10	0.80	15.8	14.2	21.7		1.25	5.62		13.3
	0.81	15.5	13.9	21.5	0.10	1.26	5.50		13.2
-0.09	0.82	15.1	13.6	21.3		1.27	5.37		13.1
-0.08	0.83	14.8	13.3	21.0		1.28	5.24		12.9
	0.84	14.5	13.0	20.8	0.11	1.29	5.13		12.8
-0.07	0.85	14.2	12.8	20.6		1.30	5.01		12.6
	0.86	13.8	12.4	20.4		1.31	4.90		12.5
-0.06	0.87	13.5	12.1	20.2	0.12	1.32	4.79		12.3
	0.88	13.2	11.9	19.9		1.33	4.68		12.2
-0.05	0.89	12.9	11.6	19.7		1.34	4.57		12.1
	0.90	12.6	11.3	19.5	0.13	1.35	4.47		11.9
-0.04	0.91	12.3	11.1	19.3		1.36	4.37		11.8
	0.92	12.0	10.8	19.1		1.37	4.27		11.7
-0.03	0.93	11.7	10.5	18.9	0.14	1.38	4.17		11.5
	0.94	11.5	10.3	18.7		1.39	4.07		11.4
-0.02	0.95	11.2	10.1	18.5		1.40	3.98		11.3
	0.96	11.0	9.9	18.3	0.15	1.41	3.89		11.2
	0.97	10.7	9.6	18.1		1.42	3.80		11.0
-0.01	0.98	10.5	9.4	17.9		1.43	3.72		10.9
0.00	0.99	10.2	9.2	17.7		1.44	3.63		10.8
0.00	1.00	10.00		17.6	0.16	1.45	3.55		10.7
	1.01	9.78		17.4		1.46	3.47		10.6
0.01	1.02	9.55		17.2		1.47	3.39		10.5
	1.03	9.33		17.0	0.17	1.48	3.31		10.3
	1.04	9.12		16.8		1.49	3.24		10.2
0.02	1.05	8.91		16.6		1.50	3.16		10.1
	1.06	8.70		16.5	0.18	1.51	3.09		10.0
0.03	1.07	8.51		16.3		1.52	3.02		9.9
	1.08	8.31		16.1		1.53	2.95		9.7
	1.09	8.12		15.9		1.54	2.88		9.6
0.04	1.10	7.94		15.7	0.19	1.55	2.82		9.5
	1.11	7.76		15.6		1.56	2.75		9.4
0.05	1.12	7.58		15.4		1.57	2.69		9.3
	1.13	7.42		15.2	0.20	1.58	2.63		9.2
	1.14	7.25		15.1		1.59	2.57		9.1

TABLES AND CHARTS

TABLE IX (Continued)

CONVERSION TABLES

$\log E$	E	Percent- age Trans- mitted	90° Sector Angle	Polarizing Angle (45° extinction)	$\log E$	E	Percent- age Trans- mitted	90° Sector Angle	Polarizing Angle (45° extinction)
0.21	1.60	2.51		9.0	0.35	2.25	0.56		4.28
	1.61	2.45		8.9	0.36	2.30	0.50		4.05
	1.62	2.40		8.8	0.37	2.35	0.45		3.82
	1.63	2.34		8.7	0.38	2.40	0.40		3.62
	1.64	2.29		8.6	0.39	2.45	0.36		3.42
0.22					0.40	2.50	0.32		3.22
	1.65	2.24		8.5	0.41	2.55	0.28		3.05
	1.66	2.19		8.4		2.60	0.25		2.87
	1.67	2.14		8.3	0.42	2.65	0.22		2.72
	1.68	2.09		8.2	0.43	2.70	0.20		2.55
0.23	1.69	2.04		8.1					
					0.44	2.75	0.18		2.42
	1.70	2.00		8.03	0.45	2.80	0.16		2.28
	1.71	1.95		7.95		2.85	0.14		2.15
	1.72	1.91		7.87	0.46	2.90	0.13		2.03
0.24	1.73	1.86		7.76	0.47	2.95	0.11		1.92
	1.74	1.82		7.68					
					0.48	3.00	0.10		1.82
	1.75	1.78		7.60		3.04	0.09		1.72
	1.76	1.74		7.51	0.49	3.10	0.08		1.62
0.25	1.77	1.70		7.43	0.50	3.15	0.07		1.51
	1.78	1.66		7.33		3.20	0.06		1.43
	1.79	1.62		7.25	0.51	3.25			1.36
					0.52	3.30	0.05		1.28
	1.80	1.58		7.18		3.35			1.21
0.26	1.81	1.55		7.10	0.53	3.40	0.04		1.14
	1.82	1.51		7.02	0.54	3.45			1.08
	1.83	1.48		6.93					
	1.84	1.45		6.85		3.50	0.03		1.02
					0.55	3.55			0.97
0.27	1.85	1.42		6.78		3.60			0.91
	1.86	1.38		6.70	0.56	3.65			0.86
	1.87	1.35		6.62	0.57	3.70	0.02		0.81
	1.88	1.32		6.55		3.75			0.76
	1.89	1.29		6.48	0.58	3.80			0.72
0.28						3.85			0.68
	1.90	1.26		6.40	0.59	3.90	0.01		0.64
	1.91	1.23		6.33		3.95			0.60
	1.92	1.20		6.25	0.60	4.00			
	1.93	1.17		6.18	0.65	4.50			
0.29	1.94	1.15		6.12	0.70	5.00			
					0.74	5.50			
	1.95	1.12		6.05	0.78	6.00			
	1.96	1.10		5.98					
	1.97	1.07		5.92	0.81	6.50			
0.30	1.98	1.05		5.85	0.85	7.00			
	1.99	1.02		5.78	0.88	7.50			
					0.90	8.00			
					0.93	8.50			
	2.00	1.00		5.72		9.00			
0.31	2.05	0.89		5.40	0.95	9.50			
0.32	2.10	0.79		5.10	0.98	10.00			
0.33	2.15	0.71		4.82	1.00				
0.34	2.20	0.63		4.54	∞	∞			

SPECTRUM CHARTS

The following plates (Plates II to XXXVI) are of the iron spectrum from 2310 to 5090 \AA with identified iron lines and indicated position of the principal lines of other elements.

The blank space above the iron spectrum is intended for use as a projection screen or for the superposition of an enlarged strip of the unknown spectrum and adjacent iron comparison spectrum. The vertical lines in this blank space are extended lines for a few of the unknown elements so as to permit vertical alignment of the projected spectrum lines.

In order to fill the pages a different reduction was used on some of these plates as compared with others. This change in reduction size is particularly noticeable between the series of Plates II to XXVII and the series of Plates XXVIII to XXXVI.

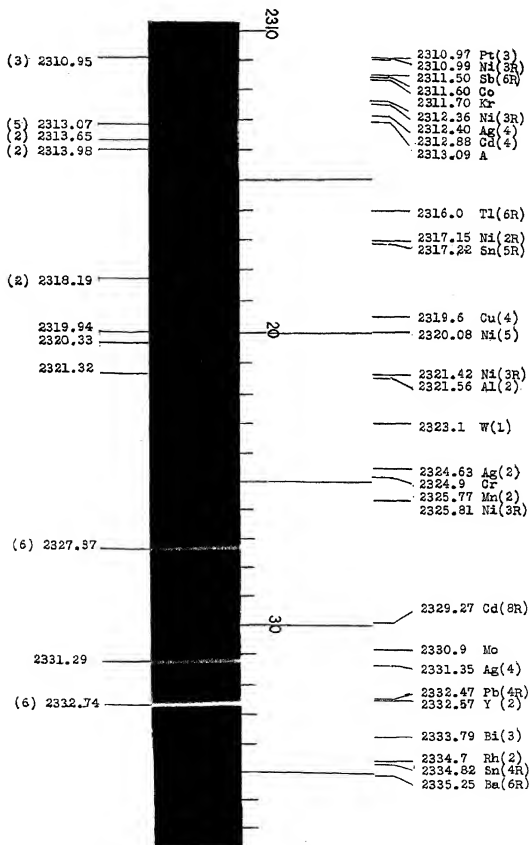


PLATE III

2330-2360A

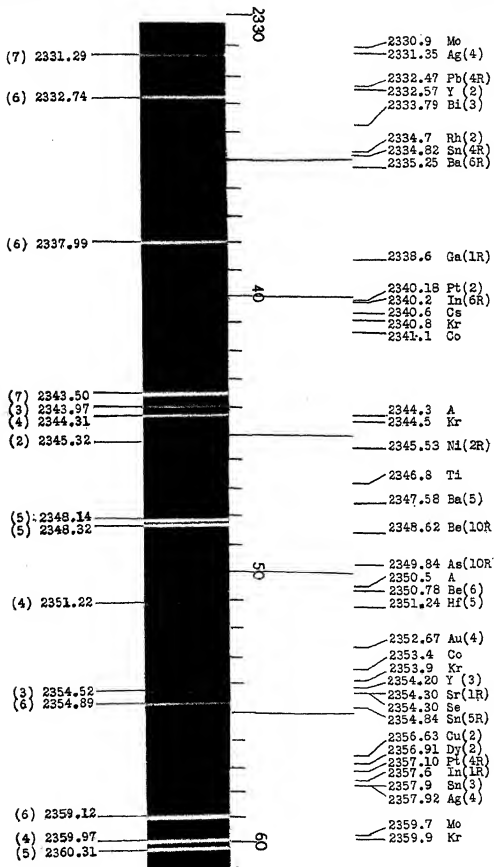


PLATE IV

2360-2390A

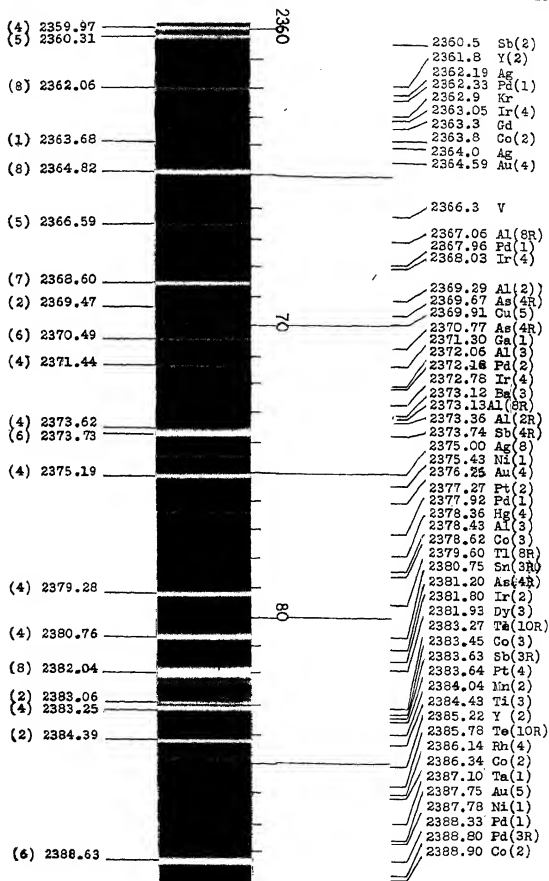


PLATE V

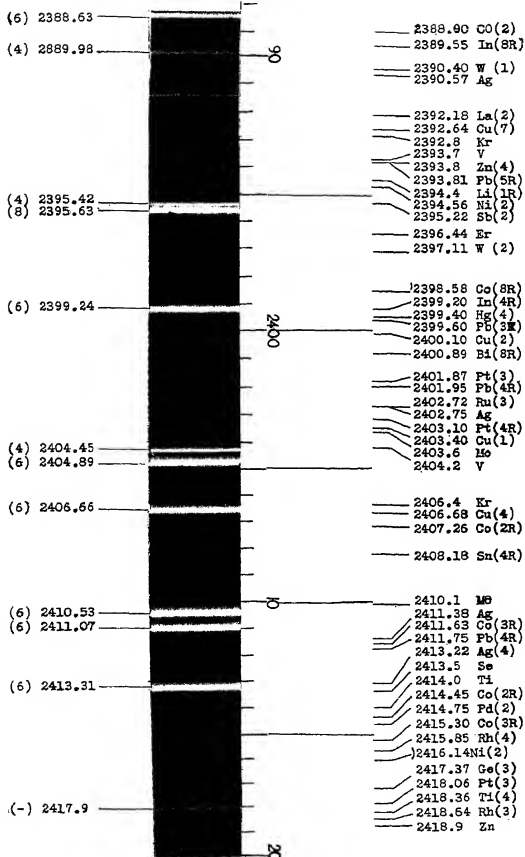
2390-2420 μ 

PLATE VI

2420-2452A

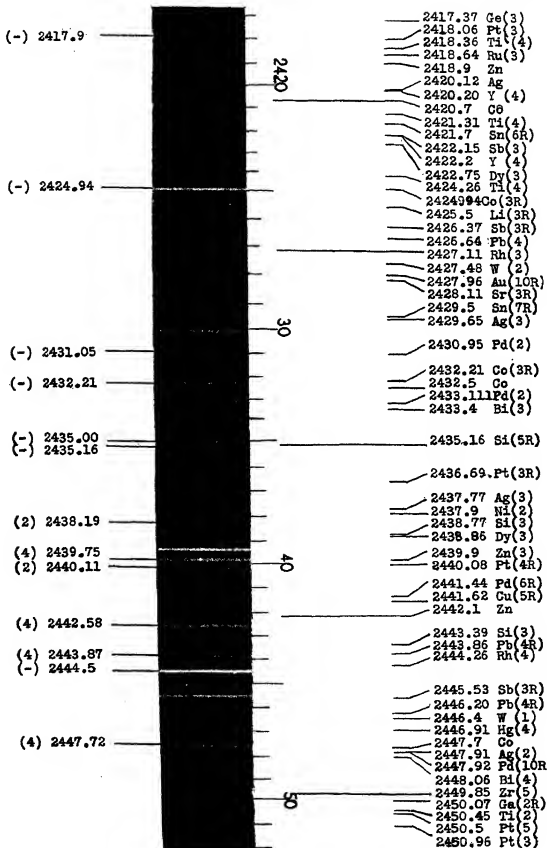


PLATE VII

2452-2487A

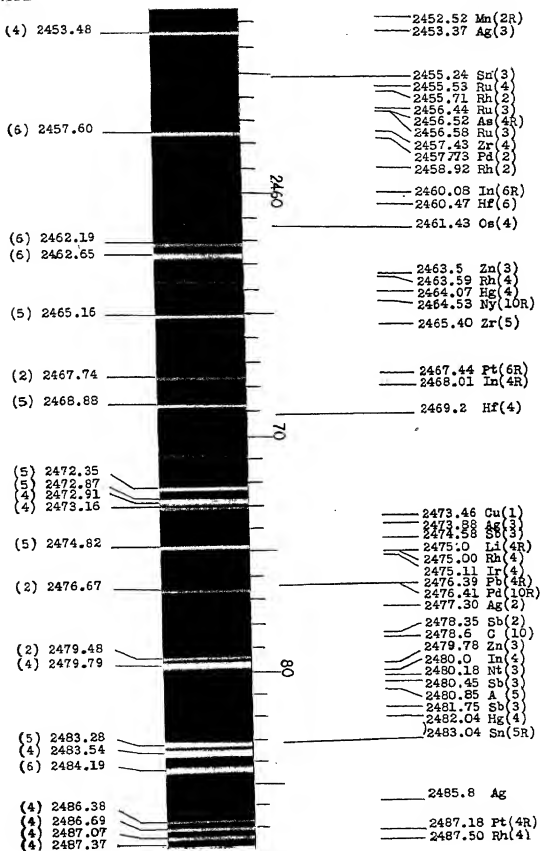


PLATE VIII

2487-2520Å

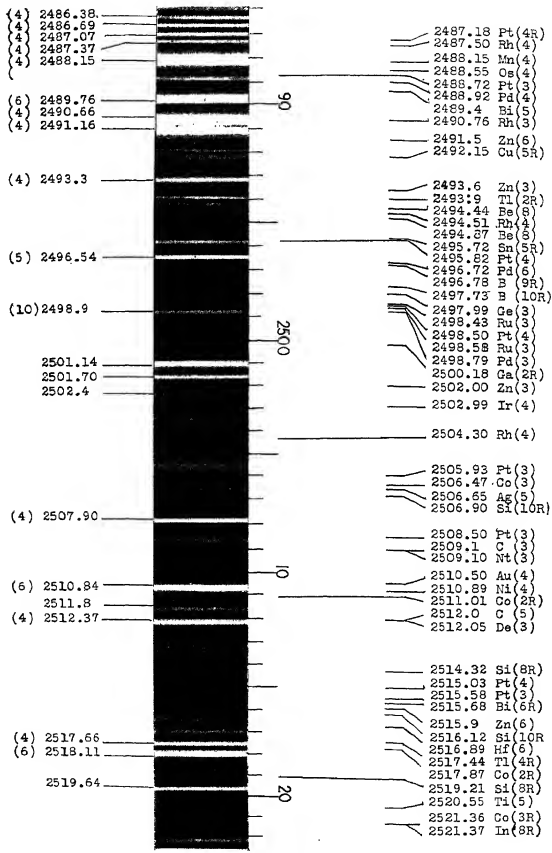


PLATE IX

2520-2555A

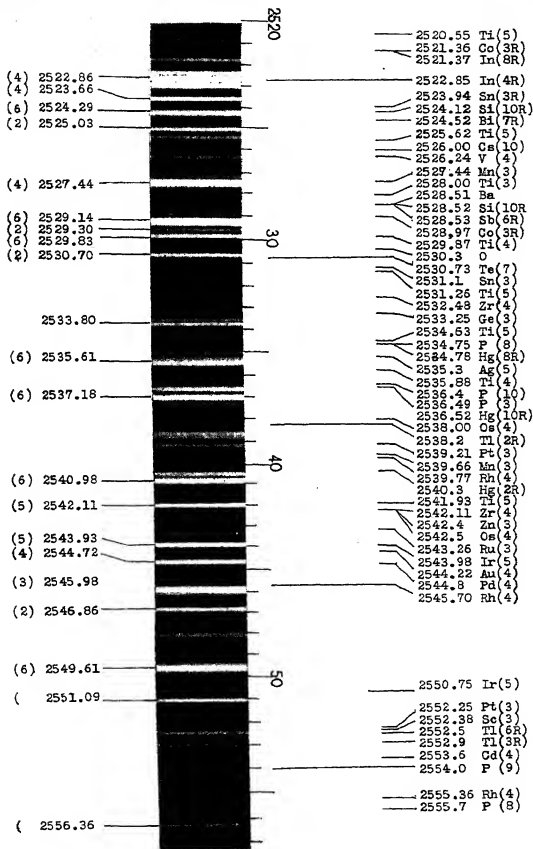
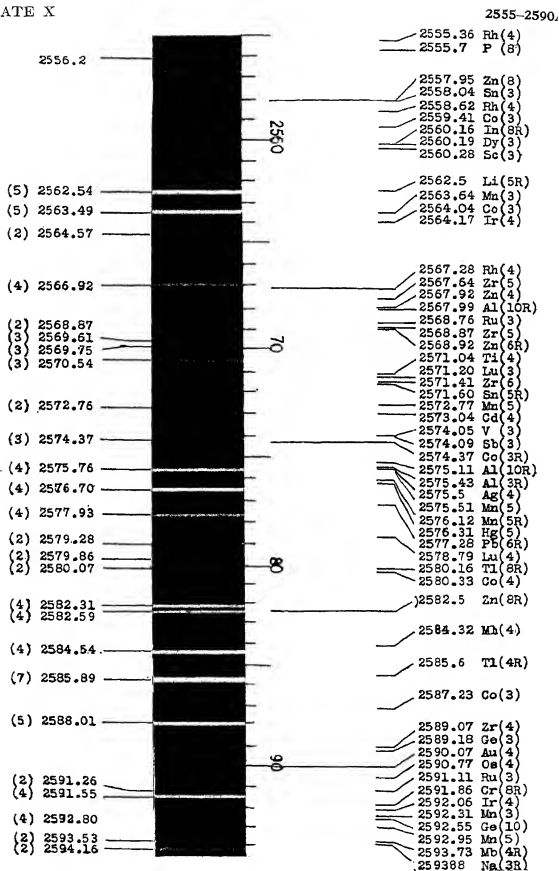


PLATE X



SPECTRUM CHARTS

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PLATE XI

2590-2630

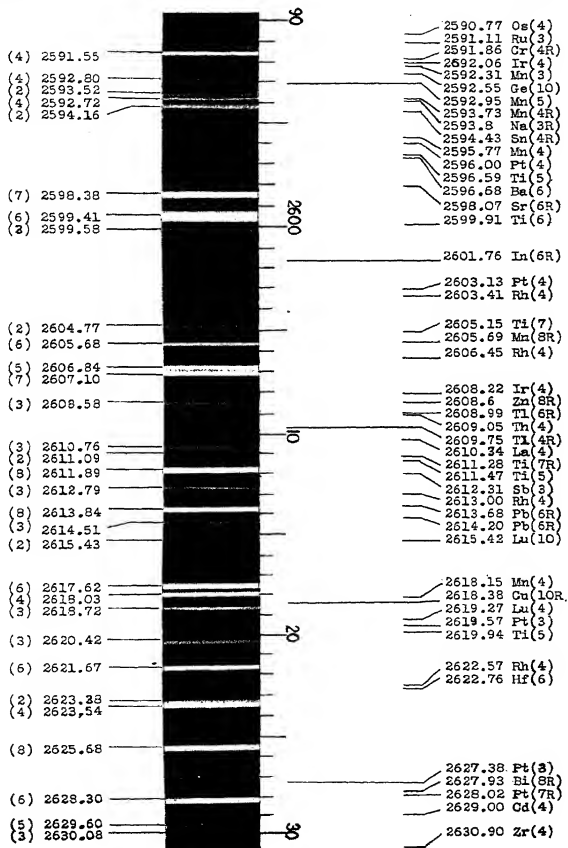


PLATE XII

2630-2668A

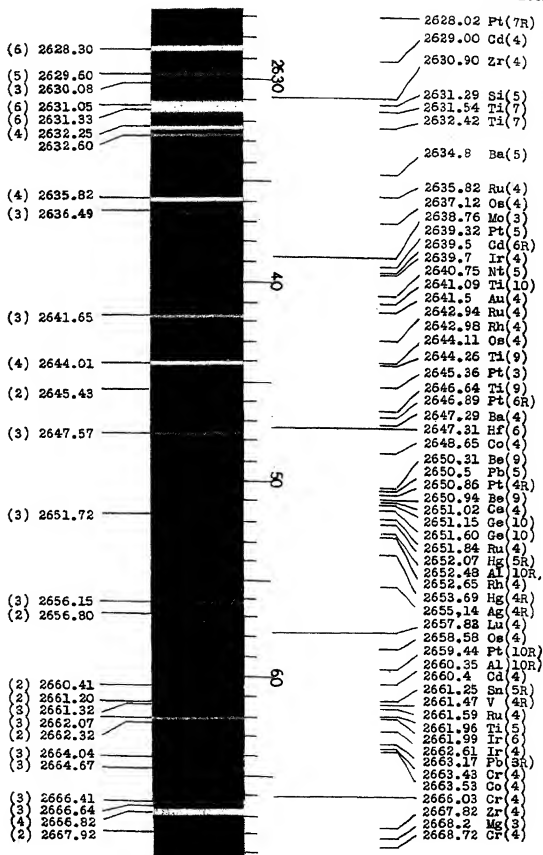


PLATE XIII

2712-2755A

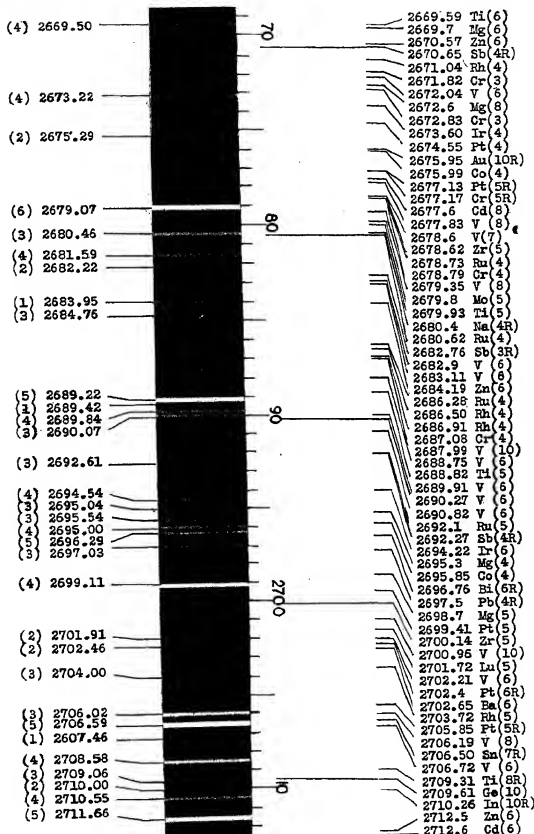


PLATE XIV

2669-2712A

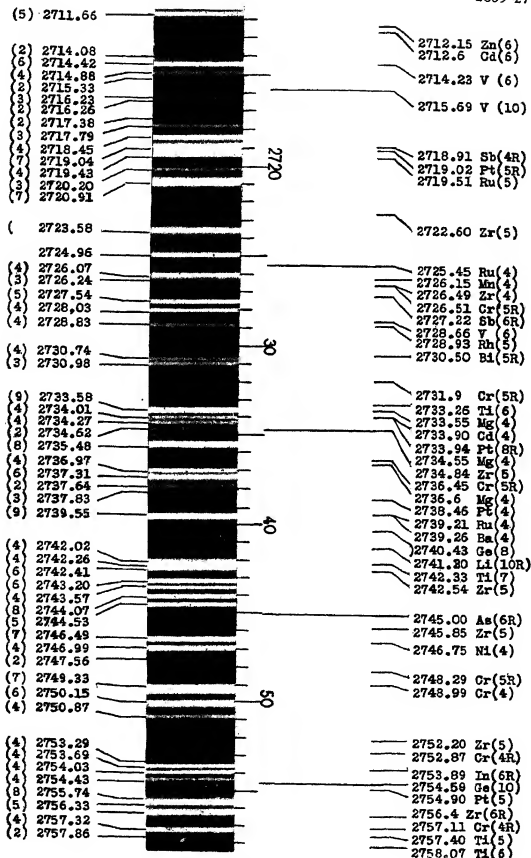
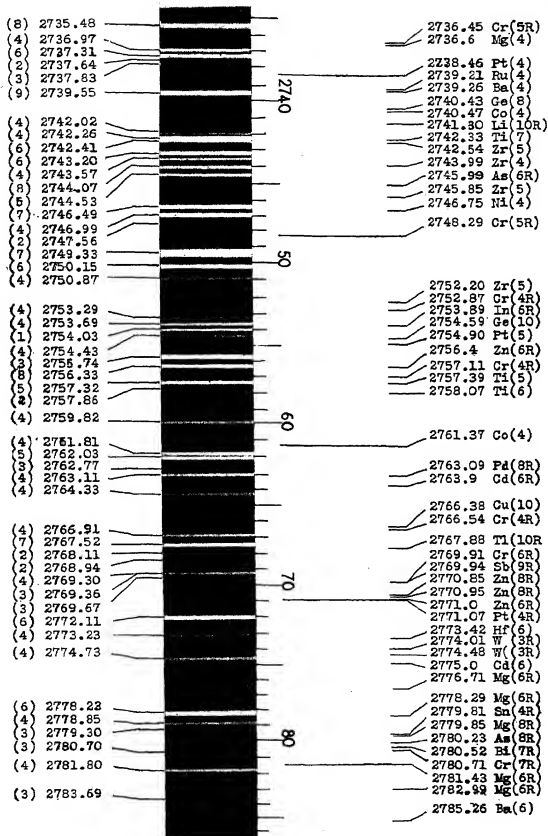


PLATE XV

2735-2785A



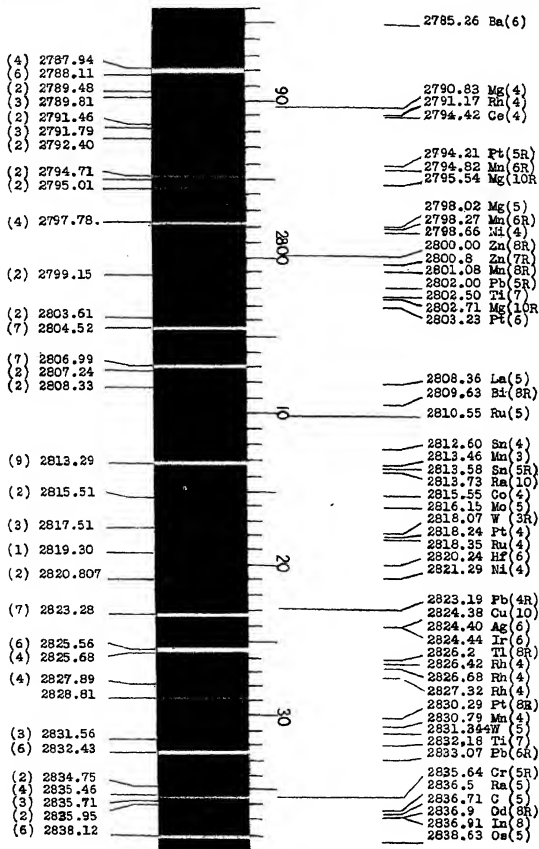


PLATE XVII

2738-2890A

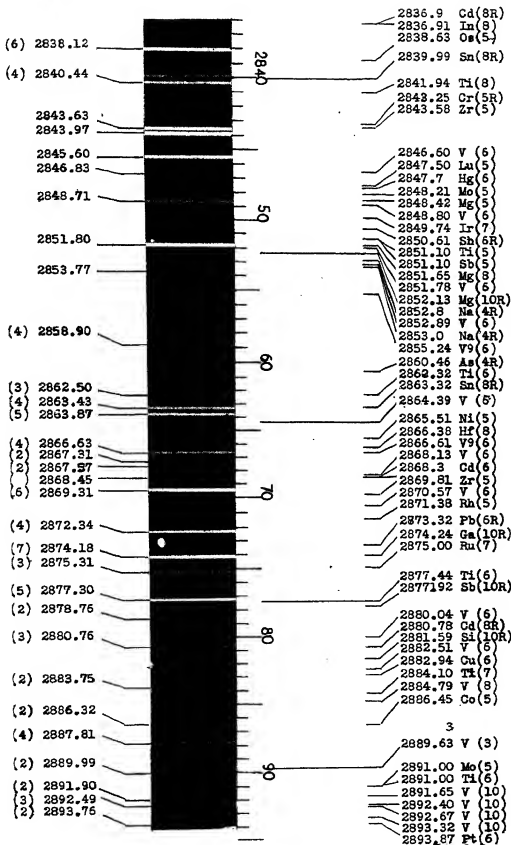


PLATE XVIII

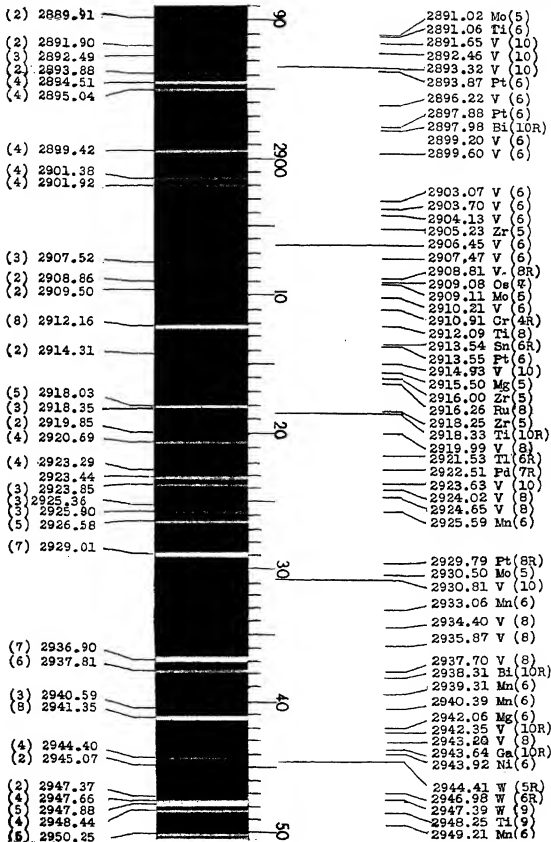
2890-2950_Å

PLATE XIX

2950-3010A

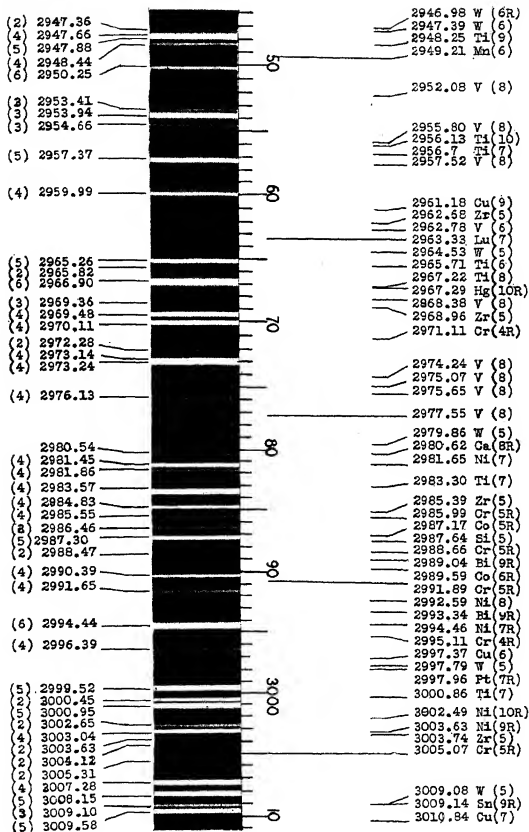


PLATE XX

3005-3065A

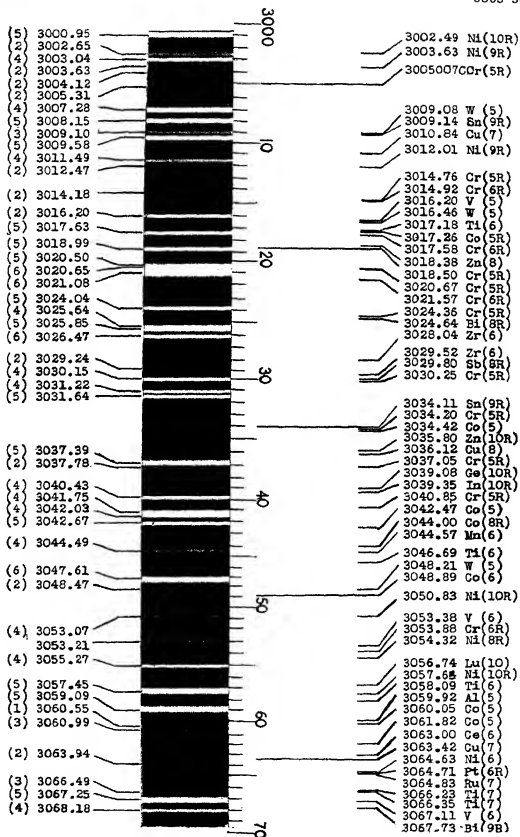
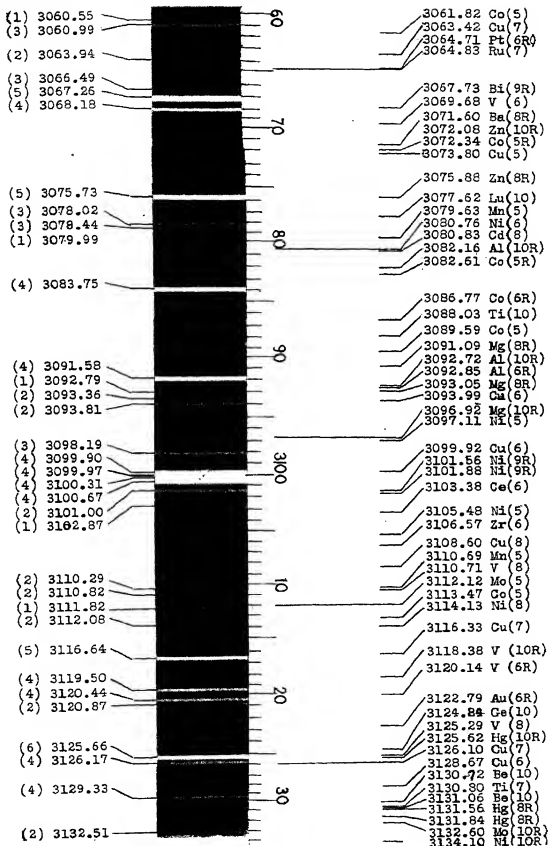


PLATE XXI

3060-3130A



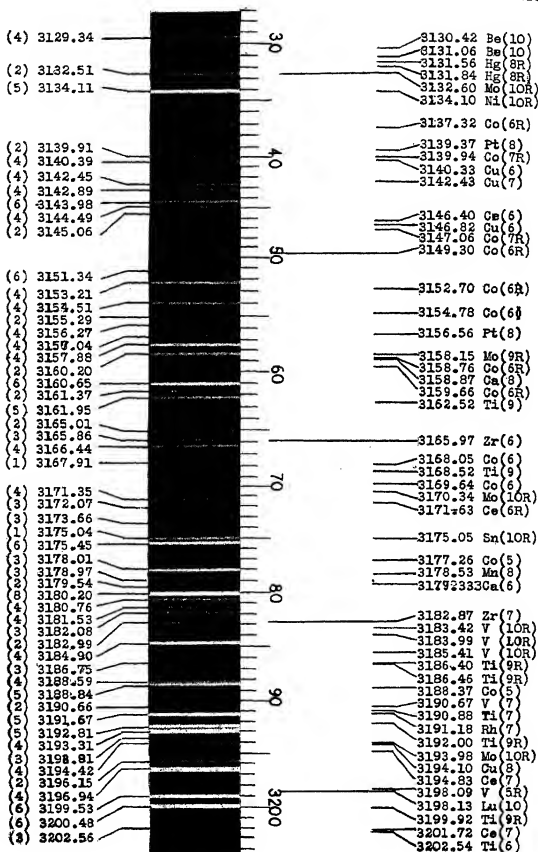
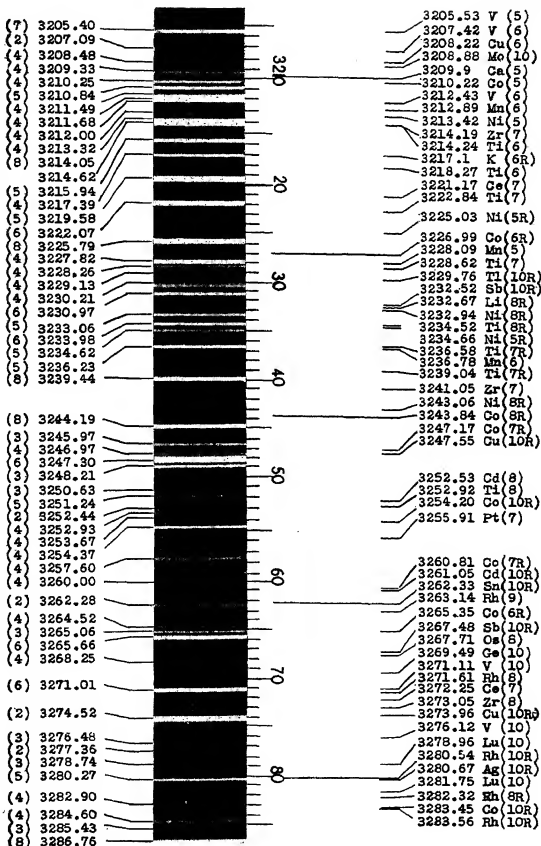


PLATE XXIII

3105-3280A



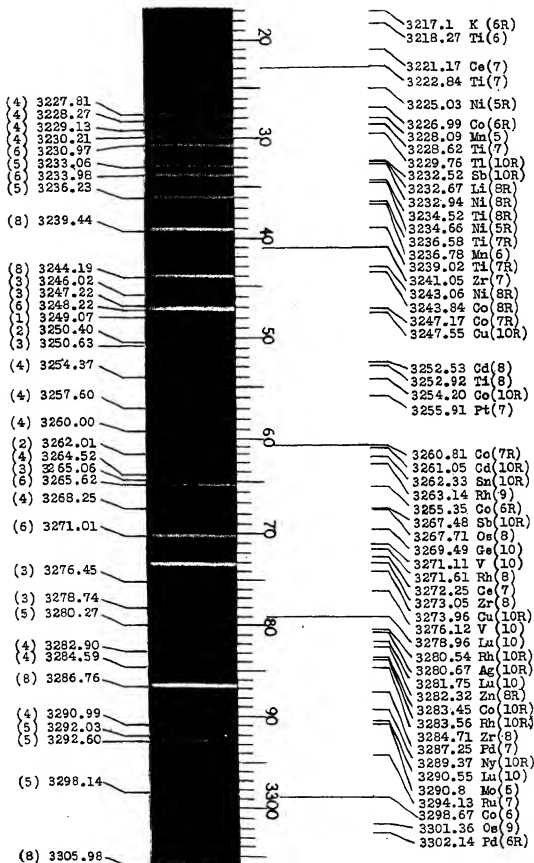


PLATE XXV

3300-3395A

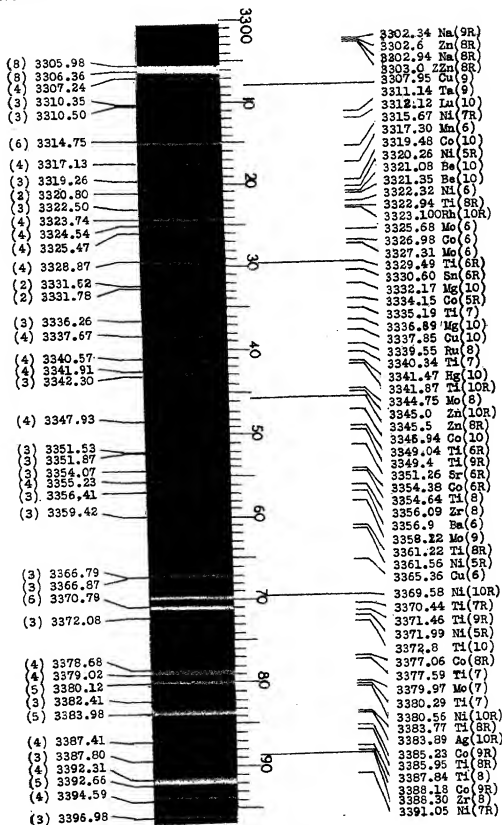


PLATE XXVI

3395-3490A

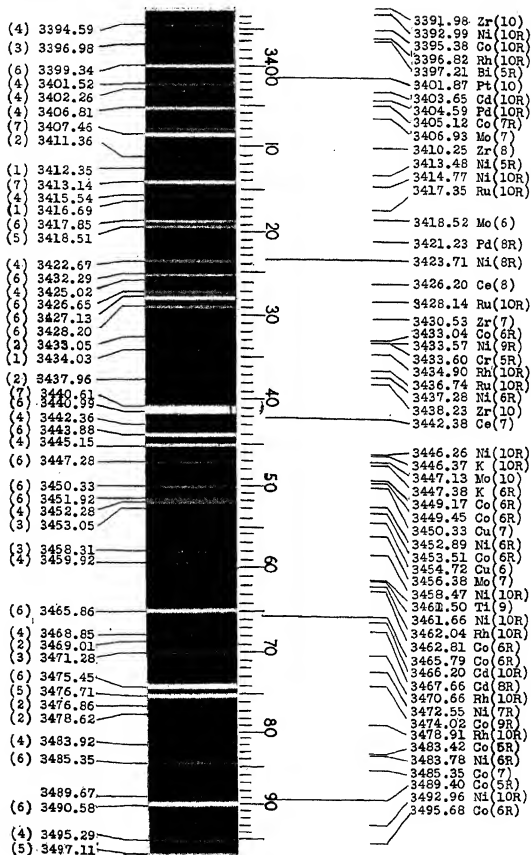
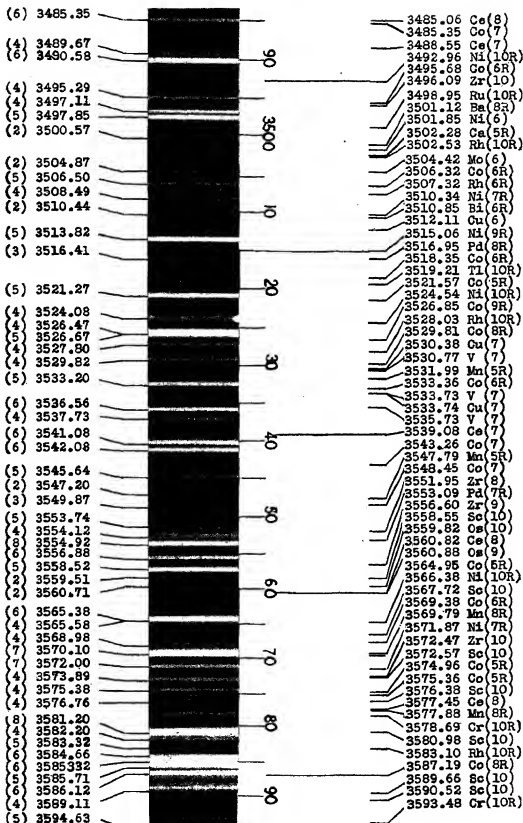


PLATE XXVII

3490-3595A



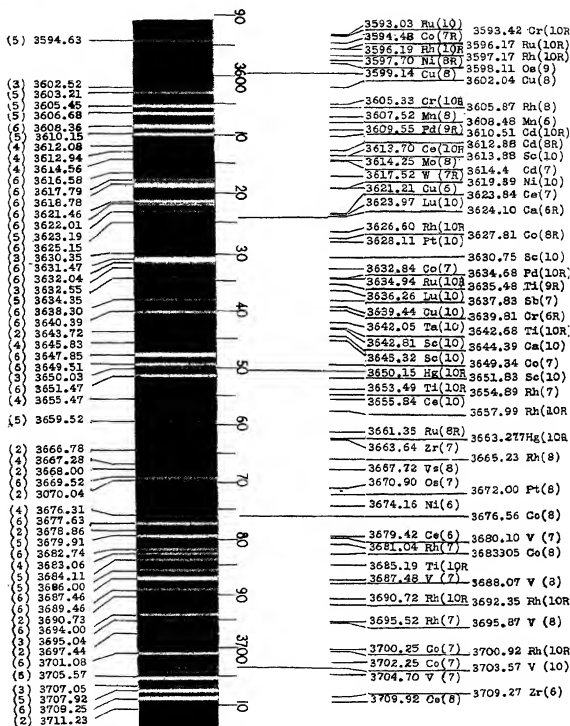
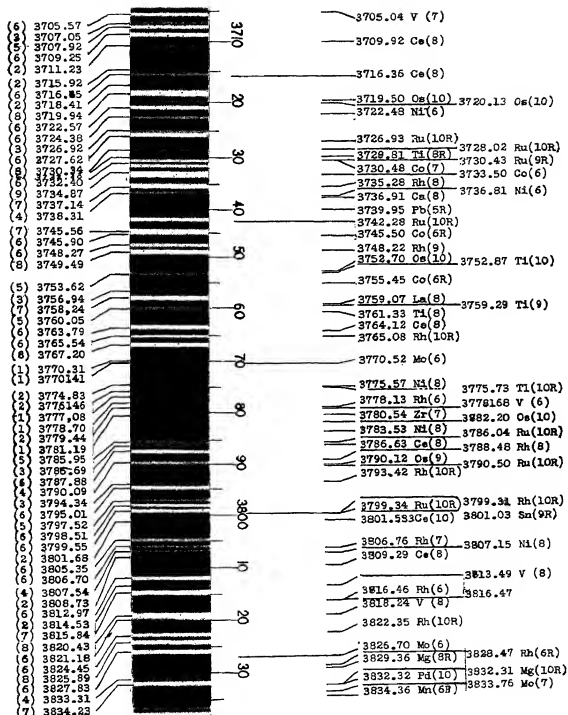
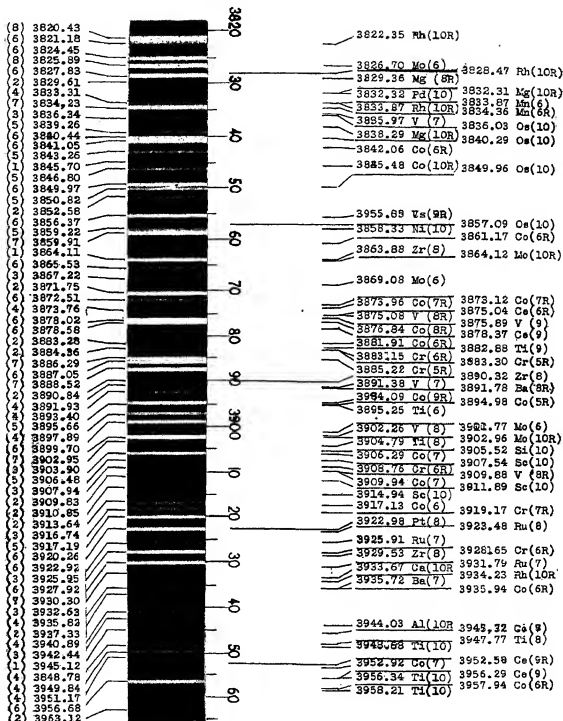


PLATE XXIX

3710-3830A





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PLATE XXXI

3950-4100A

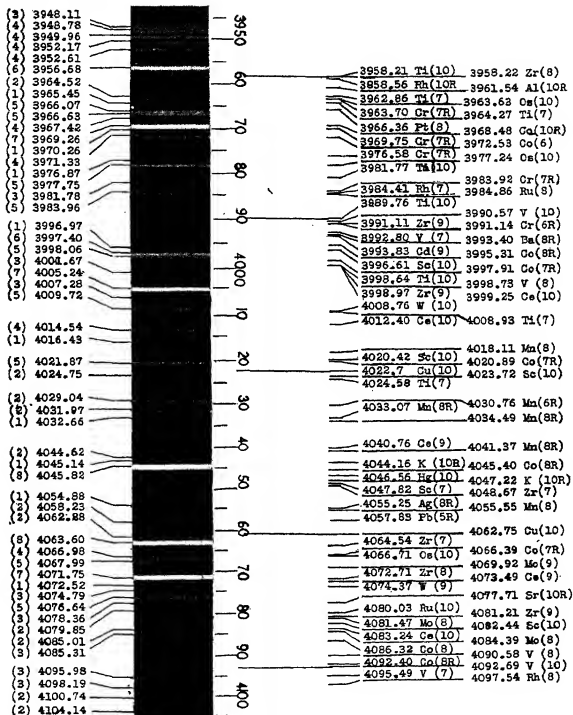


PLATE XXXIII

4200-4400A

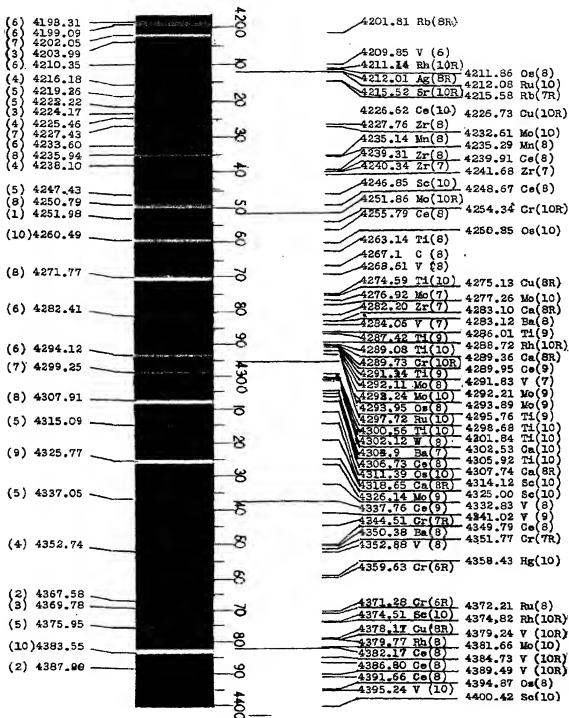


PLATE XXXIV

4400-4630A

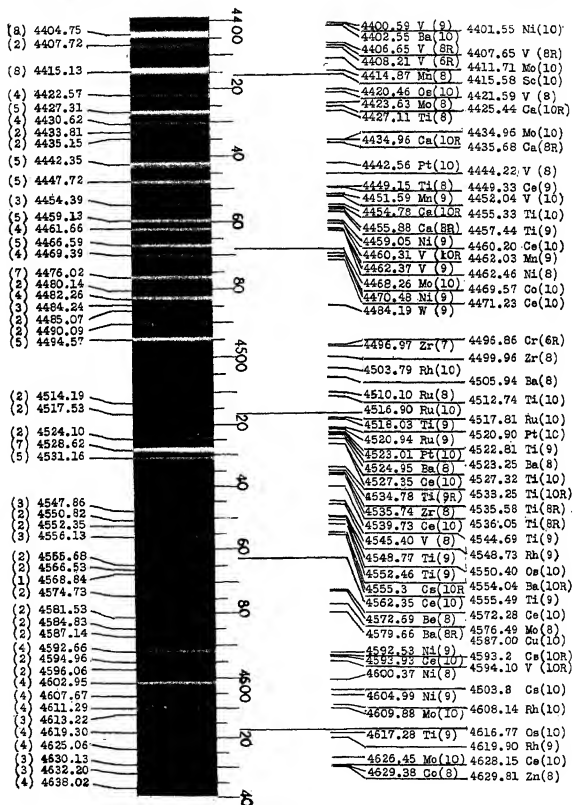
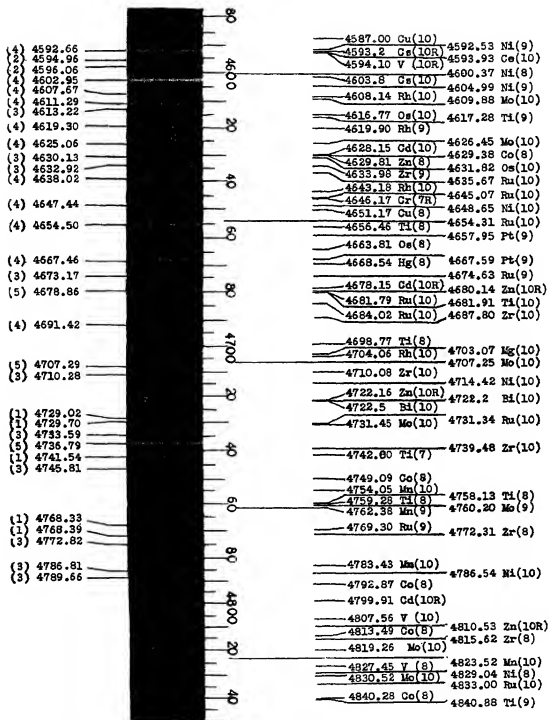
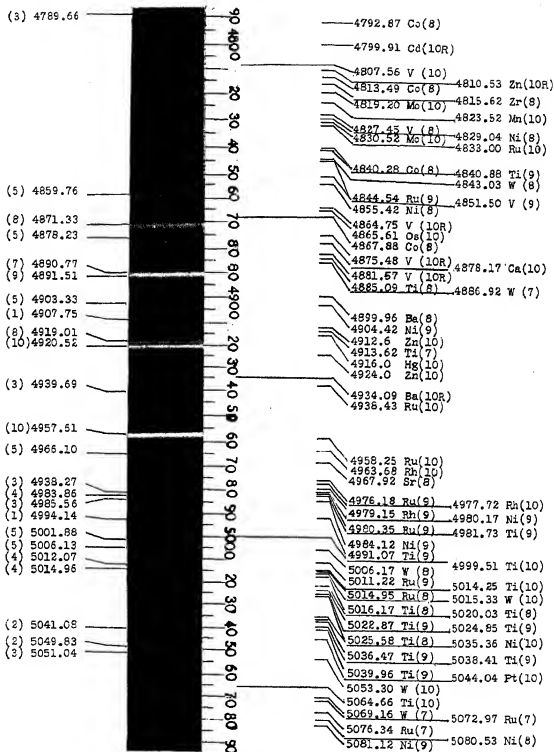


PLATE XXXV

4600-4840A





INDEX OF SYMBOLS

(Definitions of common symbols are given on the indicated pages.)

- A (angstrom), 4
- A (absorption), 226
- c (concentration), 4
- c (velocity of light), 4, 191
- cm^{-1} , (unit of wavenumber), 4
- d (electron configuration), 16
- d (thickness), 4
- D (series term), 11
- E (energy), 7, 23
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- ϵ (molecular extinction), 4
- f (fresnel), 4, 191
- f (electron configuration), 16
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